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The Journal
of the
SOCIETY OF DYERS AND COLOURISTS

Volume 68 Number 2

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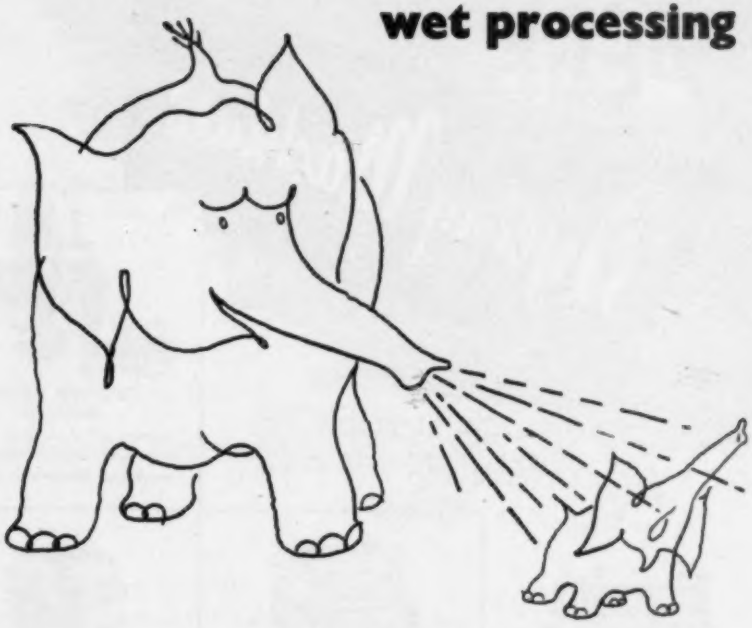

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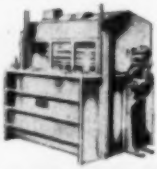

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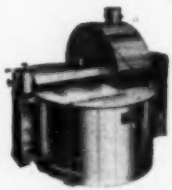

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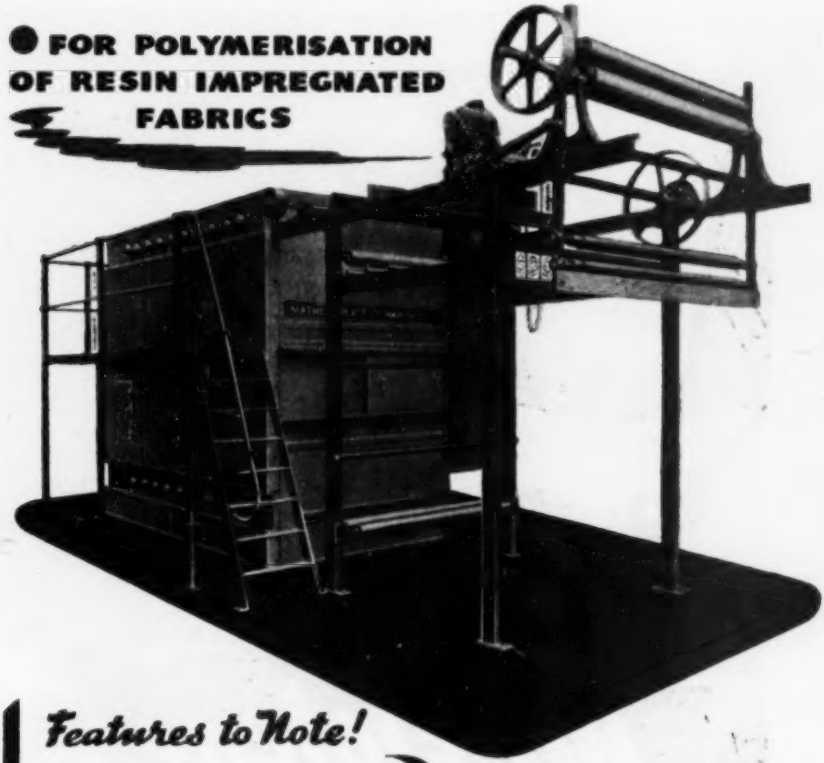

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1952 and pages 253–256 of the July 1951 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, 19 Piccadilly, Bradford, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

COMMUNICATIONS

Package Dyeing—
I—A Theoretical Model and its relation to Technical Practice — *J. Boulton and J. Crank*

The Action of β-Propiolactone on Wool — *C. Fearnley and J. B. Speakman*

Studies in the Fundamental Processes of Textile Printing.
III— The Transfer of Acid Dyes to Cellulose during Steaming — *R. B. Patel and H. A. Turner*

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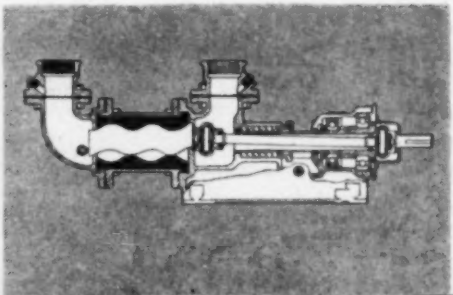

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Forthcoming Meetings of the Society

Friday—7th March 1952 at 7-30 p.m.

Second George Douglas Lecture Dr. R. Hill *Synthetic Fibres in Prospect and Retrospect* Midland Hotel, Manchester

Friday—28th March 1952

ANNUAL GENERAL MEETING and DINNER of the Society Queens Hotel, Leeds

Friday—9th May 1952

Ninth Mercer Lecture Dr. F. C. Wood *Non-felting Wool and Wool Mixtures* College of Technology, Leicester

HUDDERSFIELD SECTION

All meetings held at Field's Café, Huddersfield at 7.30 p.m., unless otherwise stated.

1952

Tuesday 18th March — Dr. C. B. Stevens *Some Observations on Dyeing Properties of Modified Wool*

Tuesday 8th April — ANNUAL GENERAL MEETING Dr. G. H. Lister (Sandoz Products Ltd.) *Acid and Chrome Dyes on Wool*

LONDON SECTION

All meetings held at 6 p.m. in the Rooms of the Royal Society, Burlington House, Piccadilly, London W.1, unless otherwise stated

1952

Friday 7th Mar. — Three short papers followed by a questionnaire on *Problems of the Garment Dyer and Cleaner*

It is also intended to hold a Dinner and Dance in the New Year, and to arrange for a lecture to be given in Luton in the spring, on a subject of interest to the hat industry. The date for the Annual General Meeting will be fixed later, for some time shortly after the last meeting of the session.

MANCHESTER SECTION

1952

Thursday 6th March — (Joint with the Textile Institute, Lancashire Section), Dr. A. Landolt (Ciba Ltd.) *Modern Developments in Textile Auxiliaries.* Textile Institute. 7 p.m.

Friday 21st March — Symposium on *Systems of Pack Dyeing*. Gas Showrooms, Town Hall Extension, Manchester. 6.30 p.m.

Friday 18th April — Annual General Meeting, details to be announced later. Gas Showrooms, Town Hall Extension, Manchester. 6.30 p.m.

MIDLANDS SECTION

All meetings commence at 7 p.m.

1952

Friday 22nd Feb. — MIDLANDS SECTION DINNER Black Boy Hotel, Nottingham

Continued on page xxv

Midlands Section—*continued*

Wednesday 27th Feb. — G. G. Taylor, Esq., B.Sc., A.Inst.P. *The Uses of Microscopy in Textile Dyeing and Finishing* (Joint Meeting with the British Association of Chemists). Midland Hotel, Derby

Wednesday 26th March — G. H. Lister, Esq., Ph.D., B.Sc. *The Influence of Dyeing Methods on Fibre Damage.* College of Technology, Leicester

Wednesday 23rd April — G. K. Mecklenburgh, Esq., S. Shaw, Esq., and H. W. Peters, Esq. *Some Developments in Setting and Finishing Nylon Textiles* (Preceded at 6.45 p.m. by the Annual General Meeting of the Section). King's Head Hotel, Loughborough

NORTHERN IRELAND SECTION

All meetings to be held in Queen's Hotel, Belfast at 7.30 p.m.

1952

Thursday 6th March — R. C. McKinney, Esq. (Lilliput Laundry and Dyeworks Ltd.) *Commercial Laundering in Practice* (Joint Meeting with Textile Institute)

Saturday 5th April — ANNUAL GENERAL MEETING and DINNER Queen's Hotel, Belfast A.G.M. 5 p.m. Dinner 6.30 for 7 p.m.

SCOTTISH SECTION

All meetings at 7 p.m., St. Enoch Hotel, Glasgow

1952

Tuesday 18th March — ANNUAL GENERAL MEETING 7 p.m. LECTURE 7.30 p.m. J. Zonnenberg, Esq. *Recent Developments in Starch Products and their application to Sizing, Finishing and Printing*

BRADFORD JUNIOR BRANCH

All meetings held in the Bradford Technical College at 7.15 p.m.

1952

Thursday 28th Feb. — THE JUNIOR BRANCH DANCE at the Queen's Hall

Wednesday 5th March — J. A. Hepworth, Esq., B.Sc., A.T.I. (Shell Chemicals Ltd.) *Petroleum Derived Chemicals in the Textile Industry*

Saturday 8th March — Visit to Wool Industries Research Association, Torridon

Tuesday 25th March — E. E. Tallis, Esq., B.Sc., A.R.I.C. (Courtaulds Ltd.) *Recent Developments in Viscose Rayon and Staple Manufacture*

There will be a visit to Salts (Saltaire) Ltd., the date of which has not yet been fixed.

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THE JOURNAL
OF THE
Society of Dyers and Colourists

Volume 68—Number 2 FEBRUARY 1952 *Issued Monthly*

Proceedings of the Society

The pH Control of Acid and Chrome Dyeing
II—Single-bath Mordant Dyeing

G. H. Lister

Meetings of the West Riding Section held at the Great Northern Victoria Hotel, Bradford, on 9th February 1950, Mr. J. M. Goodall in the chair; and of the Scottish Section held at the St. Enoch Hotel, Glasgow, on 17th October 1950, Mr. E. D. Kennedy in the chair

The results of the use of pH control of dyebaths in bulk dyeing are summarised. The re-use of dyebaths in order to save fuel is discussed. The metachrome process is examined, and suggestions are made for the prevention of high pH in enclosed machines. The effect of temperature on chrome lake development is described. Other single-bath chrome mordant dyeing methods have been investigated, together with processes for the inactivation of chromates and dichromates in dye liquors.

Following an examination in the laboratory of the behaviour of twelve dyes towards change in concentration of acid in the dyebath, it was suggested that dyeings in bulk might be improved from the point of view of level dyeing, and an appreciable saving in dyeing time brought about, if a modified technique of applying the dyes were used[1]. The general conclusions were that, with the exception of dyes of the type of Xylene Light Yellow 2G, Azo Rhodine 2G, and Alizarine Light Blue B, migration is insufficient to bring about levelling of an initially uneven dyeing in reasonable dyeing time. Migration is slow compared with absorption, and it is desirable to ensure that the initial strike of the dye is even rather than to depend upon migration to obtain an even result. It was argued, therefore, that if the strike is even, it is unnecessary to continue boiling for long periods in order to obtain satisfactory results. Strike is controlled by the pH of the dyebath.

Since the preliminary work, over two hundred dyes have been examined, and the best pH for dyeing each of them has been determined. In addition, the principles and methods have been applied to the bulk dyeing of loose wool, slubbing, yarn in hank and cheese, piece goods, and wool hose.

As a result of the examination of the larger number of dyes, it has been necessary to modify some conclusions. Thus the change in percentage exhaustion per unit of pH in the region of 50% exhaustion is not 30% for all dyes, but varies from 20% to 35%, the sensitivity decreasing as anion affinity increases; i.e. the less level dyeing dyes are less sensitive to change in pH.

The results obtained in bulk will be the subject of a separate communication elsewhere, and it is only intended here to summarise them.

In the standard technique, the material is pretreated with acid at 60–70°C. in the absence of dye to give the optimum pH for dyeing. When this is obtained, normally after 15 min., the dye solution is entered, the bath raised to the boil in 20 min., and boiling continued for 20 min., when satisfactory exhaustion and a level result should have been obtained. If required, chroming may then be carried out.

On loose wool, slubbing, and cheese in pressure dyeing machines the results have been excellent with both acid milling and afterchrome dyes. In addition, slubbing has been dyed satisfactorily in Calvert machines.

Results on yarn in hank form, particularly with the level dyeing acid dyes, have varied. Generally, circulation is not as good as in pressure dyeing machines, and it was necessary to use control of temperature as well as pH. In addition, level dyeing acid dyes are probably the most selective when dyeing blended wools, and some of the results obtained, while overall level, have been skittery and have required boiling to get solidity. Because of the supply position, experience with the technique on yarn has been limited. Satisfactory results have been obtained, however, by pretreating at the boil and entering dye at the boil using standing baths. It is apparent that, while the general principles still hold good for yarn, local conditions may have to be studied before the method can be recommended at a particular dyehouse.

Work on piece again has been limited by lack of supplies. In addition, when a shade has to be matched accurately, a number of saltings may be required, and an economy of 30–60 min. in dyeing time is not so important. Better results compared

with normal dyeing methods were obtained, however, by pH control at the end of equivalent times from the point of view of penetration and levelness.

To summarise, on loose wool, slubbing, and cheese the method shows considerable advantage. On yarn success depends somewhat on local conditions and the type of dyes used, while on piece insufficient data are available to draw conclusions, but such evidence as is available is favourable.

The results of the application of pH control to bulk dyeings were encouraging in that they resulted in increases in production in the dyeing of loose wool and slubbing of 20–50% depending on the previous efficiency of the dyehouse. Work was undertaken in the laboratory to discover what further improvements could be brought about in the light of bulk findings. One obvious source of loss of time in dyeing is the delay in raising the dyebath from the temperature of cold water to 60°C., particularly when all machines are drawing steam at the same time. Few dyehouses are equipped to supply hot water to dye vessels. A possible solution of this problem appeared to be to use standing baths, since this technique is successfully applied in many instances when acid dyes are applied to yarn. One defect, however, is obvious. The majority of dyes applied to loose wool and slubbing are afterchrome dyes with poor metachrome dyeing properties. In these circumstances, therefore, the re-use of a spent dye-liquor containing unexhausted dichromate would not be possible. However, three alternative possibilities have been examined—(1) Metachrome dyeing might be carried out using spent liquors. (2) Use of Chromosol Mordant would increase the number of dyes which can be applied by a single-bath process. (3) The dichromate present in the spent dye liquor might be converted into some inactive state which would not form a chrome lake in the dyebath on the addition of a non-metachrome dye.

1. THE METACHROME DYEBATH

Peryman [2] has called attention to the fact that, contrary to accepted beliefs, the pH of a dyebath containing metachrome mordant does not fall during the course of a dyeing but rises to values as high as 9. Gaunt [3] has confirmed that, when dyeing is carried out under conditions which do not allow ammonia to escape freely, high pH values arise from the metachrome dyeing process. Additional data obtained from a number of other dyehouses are in agreement with those of Gaunt, the final pH in each case being influenced by the alkaline state of the material before dyeing, the amount of metachrome mordant used, the time of boiling, and the type of machine used. It was necessary, therefore, to examine whether the material was damaged by these high pH values.

Wool yarn (10 g.) was treated under reflux at the boil for 1 hr. in water (500 ml.) containing the additions shown in Table I. The initial and final pH values of the liquors were measured with a glass electrode. The tensile strengths of single strands of the yarn in its wet state were compared with that of a sample of yarn which had merely been wetted out. The results given in Table I represent the averages of 100 tests, and the standard deviations are also given.

TABLE I

Addition	Initial pH	Final pH	Breaking Load (oz.)
Original wool (wet) ...	—	—	11·87 ± 0·15
No addition	6·90	7·70	11·02 ± 0·15
1% Potassium chromate	7·43	9·31	10·44 ± 0·17
1% Potassium chromate 2% Ammonium sulphate	7·28	8·85	10·84 ± 0·17
1% Potassium chromate 2% Monoammonium phosphate	6·30	6·85	11·54 ± 0·15
1% Potassium dichromate	5·58	7·4	11·40 ± 0·15

These results confirm that, if metachrome dyes are applied under conditions which do not allow ammonia to escape, high pH and damage to the fibre will result. This state of affairs, however, is not an essential feature of the metachrome process, but the unfortunate consequence of its application in particular types of machines. At the same time it should be pointed out that a rise in pH results from a normal afterchrome process, and dyes which are applied from a neutral dyebath and then afterchromed will give rise to damaged materials. According to Carlene, Rowe, and Speakman [4], when wool is mordanted with potassium dichromate, caustic alkalinity develops in the dyebath according to the following equations—

$$K_2Cr_2O_7 \rightleftharpoons 2K^+ + Cr_2O_7^{2-} \quad \text{(i)}$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \quad \text{(ii)}$$

The basic side-chains of the wool combine with the $HCrO_4^-$ ions, requiring a corresponding number of hydrogen ions to combine at the acid side-chains, thus resulting in an excess of hydroxyl ions in the solution.

Metachrome mordant is designed to convert the caustic soda into ammonia, which should be removed from the dye vessel by volatilisation. If this does not occur in practice, alternative methods are available to bring about the same result. Acetic acid may be gradually added by a drip-feed arrangement such as is frequently used when dyeing in water softened by the Permutit process and containing large amounts of sodium bicarbonate, or alternatively the ammonium sulphate in metachrome mordant may be replaced by a more efficient buffer such as monoammonium phosphate. In addition, the dichromate–chromate system itself has a reasonable buffering action below pH 7, and replacement of metachrome mordant with potassium dichromate avoids the development of high pH.

It was important to determine whether control of the pH of the metachrome dyebath would seriously affect the results obtained. What is of particular interest is the rate of development of the chrome lake. In the unchromed state many of the metachrome dyes possess good migration properties. Once the chrome lake is formed, however, migration in the fibre is negligible. Therefore, the more rapid the chrome lake formation the less level the result and the worse the penetration.

As a first step to examining the effect of a reduced pH in metachrome dyeing, a study was made of the change in adsorption of chromium with change in pH of the dyebath. Wool in hank form (10 g.) was treated for 20 min. at 90°C. in water (500 c.c.) containing varying amounts of acetic acid or sodium carbonate. A sample of the liquor was removed and cooled, and the pH determined. The liquor was returned to the original bath, potassium chromate was added (1% calculated on the weight of material), and the solution and wool were maintained at 95°C. for 45 min. The wool was then removed and the residual bath cooled. The pH of the liquors was determined, and also the amounts of sexivalent and tervalent chromium by Ibbotson and Howden's method [5]. The experiment was repeated using 3% of a mixture of two parts of ammonium sulphate and one part of potassium chromate (metachrome mordant) in place of potassium chromate alone.

The results (Table II) show that at equal "final pH" values above 6·5 appreciably more chromium is absorbed from the chromate–ammonium sulphate mixture than from chromate only.

TABLE II

pH after— Pretreatment	pH after— Chroming	Cr in soln.— Cr^{VI} (% of total Cr originally in bath)	Cr in soln.— Cr^{III} (% of total Cr originally in bath)	Cr absorbed by Wool (% of total Cr originally in bath)
Potassium Chromate (1% on weight of wool)				
4·18	4·64	14·0	—	86·0
4·08	4·71	19·6	0·4	80·0
4·36	5·08	23·6	3·2	73·2
5·00	5·83	42·5	1·7	55·8
4·82	6·00	47·1	1·4	51·5
5·67	6·52	50·5	3·0	46·5
5·72	6·62	50·8	3·7	45·7
8·02	7·49	60·3	5·2	34·5
8·30	8·08	55·0	17·3	28·7
8·89	8·51	54·0	21·5	24·5
9·19	8·80	52·0	25·6	22·4
Metachrome Mordant (3% on weight of wool)				
4·21	4·71	27·7	0·3	72·0
4·25	4·85	28·8	0·7	70·5
4·51	5·15	31·5	1·5	67·2
4·46	5·22	38·0	1·0	61·0
5·24	6·20	49·7	0·3	50·0
4·99	6·40	51·1	2·4	46·5
6·21	7·98	51·0	1·9	47·1
8·30	8·47	45·1	9·9	45·0
8·96	8·64	39·6	15·9	44·5
9·31	8·70	28·1	27·9	44·0

Attack on the cystine links in the wool is shown by the increases in tervalent chromium in the liquors at high pH, formation of thiol groups leading to reduction of the chromate to a chromic salt. Between pH 6 and 8·7, however, there is little change in the amount of chromium absorbed from metachrome mordant, and if rate of formation of chrome lake depends on the amount of chromium absorbed, then the metachrome process may be buffered to the lower pH without affecting level dyeing properties. Since a higher percentage of tervalent chromium is present at higher pH values, there remains the question whether this affects chrome lake formation (see p. 55).

The problem of maintaining a low pH in order to avoid fibre damage cannot be solved so simply as the above may indicate. Since most dyes with good metachrome dyeing properties also give good exhaustion from a neutral dyebath in the absence of chrome, a reduction in pH will increase the rate of exhaustion of the dye in its unchromed state. Change in rate of exhaustion with change in pH will be most marked near pH 7, as is shown by Fig. 1, which gives the exhaustions obtained after 5 min. at the boil, as determined by the technique given in Part I of this paper [1].

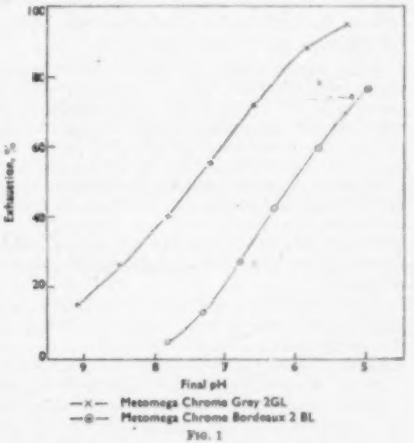

FIG. 1

Before examining in detail the metachrome dyeing process, it was necessary to establish whether the continued re-use of a metachrome dyebath, even containing dyes with good metachrome dyeing properties, would eventually lead to an accumulation of chromium lake in the dyebath of such poor solubility that staining of dye vessels would occur as well as dyeings of poor rubbing fastness. To test this, solutions containing dye and metachrome mordant were boiled together for varying lengths of time before entry of wool. The rate of absorption of the dye from these baths was then compared with the rate of absorption from a fresh bath containing the same quantities of dye and mordant as in the boiled mixture.

Although the test applied was a severe one, consisting in boiling 3% of dye in solution with 3% of metachrome mordant for 1 hr. before entry of the material, the result was satisfactory with good metachrome dyeing dyes. Differences between dyeings obtained in this way and a 3% shade obtained from a normal dyeing process were only slight. It may be expected, however, that dyes with inferior properties when applied by the normal metachrome process would show a more marked deficiency when submitted to the above process.

Most previous laboratory investigations of the metachrome process have been carried out under conditions which resulted in a fall in pH during the dyeing. It was therefore necessary to find some laboratory technique which would most closely represent the course of events in a bulk dyeing by the metachrome process. The most obvious experimental conditions were to dye under reflux at the boil. Tests of this method, however, showed that it resulted in too rapid development of the chrome lake and greater dye exhaustion than is experienced in works practice. It was then found that if dyeings were carried out in the laboratory at 95°c., exhaustion of the dyebath and rate of chrome lake formation were similar to those experienced in bulk dyeing. This condition was used in all tests except those where the effect of temperature was under investigation.

A quantitative study of the events in a metachrome dyebath is not easy. If, however, it can be shown that dye and mordant when together in the same dyebath behave independently of each other, or that the same result is obtained on the fibre whether the dye and mordant are applied separately or together, then the problem is somewhat simplified and may be examined on the fibre. In order to determine whether such an examination is legitimate, the absorptions of dye and chromium from separate baths and from the same bath were examined.

The rate of exhaustion of two dyes was determined at 90°c. (*a*) in the absence of chrome and (*b*) in the presence of 3% metachrome mordant. Residual dye was estimated colorimetrically using a sample of the original bath as standard. In order to minimise errors due to change in hue on chroming, a sample of the original bath which had been heated with metachrome mordant in the absence of wool for the same length of time was used as standard when determining the degree of exhaustion of liquors containing metachrome mordant.

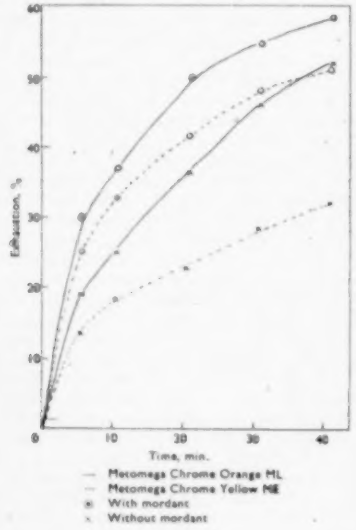

FIG. 2—90°C.

These data (Fig. 2) show that an increased rate of absorption occurs in the presence of metachrome mordant. The experiments were carried out under conditions where chrome lake formation may be expected to take place, and the effect may not be observed at lower temperatures, where chrome lake formation may take place only slowly; tests were therefore repeated at 70°c. in the same manner as before. Fig. 3 shows that, even under conditions

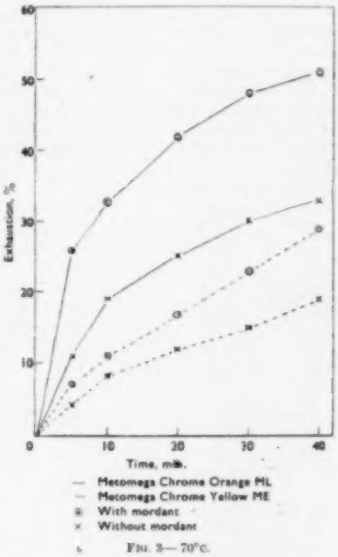

FIG. 3—70°C.

where formation of chrome lake may be expected to be slow, the presence of chromium in the dyebath still affects the absorption of the dye, indicating that some reaction between mordant and dye occurs even at this temperature.

Since the fastness to wet treatments of a chrome lake is much superior to that of the unchromed dye, the migration properties will be correspondingly inferior, and it is obviously of importance in practical dyeing to determine the properties of the dye–chromium complex which is formed at low temperatures. Carlene, Rowe, and Speakman [4] have shown that absorption of chromium by wool is independent of the presence of dye. As a first step, therefore, to examining the effect of temperature on the metachrome dyeing process, the effect of change of temperature on absorption of chrome was studied.

Wool (10 g.) was treated in water (500 ml.) containing 3% metachrome mordant for 45 min. at 50, 60, 70, 80, 90, and 100°c. (reflux). At the end of that period the amounts of sexivalent and tervalent chromium formed in the mordanting bath were

determined. The total amount of chromium present on the fibre was obtained by difference. The effect of temperatures of 50–100°C. on absorption of dye from a metachrome dyebath was also examined, the results being plotted in Fig. 4.

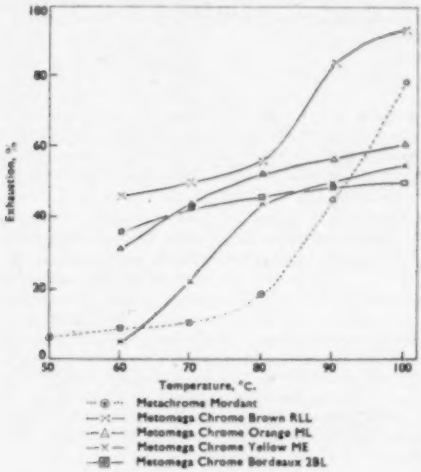

FIG. 4

The abnormal behaviour of Metomega Chrome Brown RLL which was noted throughout this work is evident from the temperature range. The general behaviour of metachrome dyes is shown by the other three dyes.

In order to determine the migration properties of the chromium compound on the fibre, it was necessary to compare them with those of a dyeing containing an equal quantity of dye applied under the same conditions, and the following technique was used.

A range of good, moderate, and poor metachrome dyes were dyed for 45 min. on wool (10 g.) at 60, 70, 80, 90°c., and under reflux at the boil, no addition being made to the dyebath. Each of the dyeings was then divided into two halves; one half was retained in its "neutral" dyed state, and the other was transferred to a fresh bath (500 ml.) containing 3% of metachrome mordant at the temperature at which the original dyeing had been carried out. The material was treated in the metachrome mordant for 45 min. Assessment of the degree of chrome lake formation was made by immersing the unchromed and chromed dyeings separately in a 1% solution of sodium carbonate (250 ml.) at 60°c. for 45 min. The colour bleeding from the chromed pattern was estimated as a percentage of the colour leaving the unchromed patterns (Fig. 5). In examining these results, it should be noted that they vary inversely as the degree of chroming; i.e. the higher the percentage colour loss the lower the percentage of chrome lake formed.

The curves in Fig. 5 show that only above 90°c. is chrome lake formation so complete that the

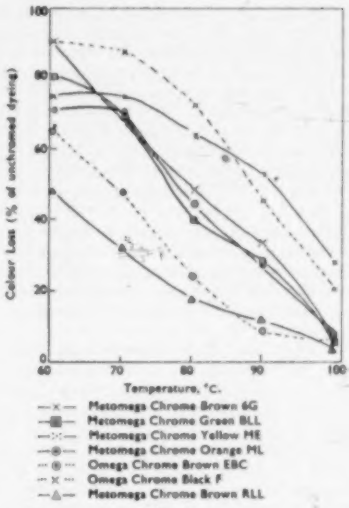
Colour Loss (% of unchromed dyeing)
Temperature, °C.
Metomega Chrome Brown 6G
Metomega Chrome Green BLL
Metomega Chrome Yellow ME
Metomega Chrome Orange ML
Omega Chrome Brown EBC
Omega Chrome Black F
Metomega Chrome Brown RLL

FIG. 5

migration properties of the complex on the fibre are markedly inferior to those of the dye in its unchromed state.

It seems possible that the smaller amount of chrome lake formed at low temperatures might be due only to the smaller amount of chromium absorbed. The experiment was therefore repeated, the amount of metachrome mordant used at each temperature being so adjusted that the quantity of chromium absorbed was equal at all temperatures to that absorbed at 90°c. The degree of chrome lake formation was assessed as before, and results are given in Table III.

TABLE III

Metomega Chrome Dye	Colour Loss (% of unchromed dyeing)				
Temperature, °c. ...	60	70	80	90	100
Yellow ME	60	60	57	55	29
Orange ML	63	53	50	28	8
Brown RLL	30	24	16	12	3

Comparison of these results with Fig. 5 shows that an increase in the amount of chromium absorbed at low temperatures results in an increase in chrome lake formation. Further work indicated, however, that low-temperature chroming, using large amounts of metachrome mordant, is not a practical possibility.

The experimental results and conclusions may be reconsidered at this stage in the light of our problems—

(a) EXTENSION OF APPLICABILITY OF SINGLE-BATH MORDANT-DYE PROCESS— Since even at low temperatures chrome and dye are able to interact to form a complex which has a more rapid rate of absorption and poorer migration properties than the unchromed dye, then mordant and dye should not be allowed to combine together until full use has been made of the slow rate of absorption and

good migration properties of the dye in its acid state. With some dyes having very poor affinity from a neutral dyebath this will involve dyeing under slightly acid conditions in order to obtain a reasonable degree of exhaustion before the entry of metachrome mordant. This method, a combination of the afterchrome and metachrome processes, will still enable the mordant to be added to the dyebath earlier than would be possible with a non-metachrome dye, and the advantage of metachrome dyeing in saving dyeing time would still be present.

Alternatively, dye and mordant may be added together at the commencement of dyeing, and the temperature raised to 80°C. and maintained there until exhaustion is almost complete; then the liquor is raised rapidly to the boil to develop fully the chrome lake.

(*b*) Re-use of Hot Spent Dye Liquors containing Chromium—Here immediate combination between the residual chrome and fresh dye is inevitable, but nevertheless the position is no more serious than is experienced in applying metachrome dyes by the method now in more general use. For the most satisfactory solution of this problem we require to find conditions where the maximum absorption of dye is accompanied by the minimum formation of chrome lake. From Fig. 4 and 5 it will be seen that these conditions are best fulfilled between 80° and 90°C., where affinity of dye for the fibre is almost equal to that at 100°C. but chrome lake formation is much more incomplete.

On this evidence the following procedure is suggested—

The spent dye liquor of known chromium content is circulated through the fresh material at 60°C. for 15 min., the requisite amount of dye added, and the temperature raised to 80–90°C. in 15 min., the dyebath is circulated for 15 min., metachrome mordant added, raised to the boil in 10 min., and boiled for 35 min., a total dyeing time of approx. 1½ hr.

(*c*) Fastness—Experiments to determine whether chroming time could be reduced without loss in fastness properties indicated that further research was required, and that recommendations would at the moment be dangerous, as the results in Table IV indicate. These were obtained by treating acid dyeings with 3% metachrome mordant at 90°C. The development of chrome lake was assessed as before, by comparing the migration of colour at 60°C. into a 1% solution of sodium carbonate, using the liquor obtained from an unchromed dyeing as a standard. A moderate and a poor metachrome dye were included in the tests for comparison.

Table IV

Dye	Colour Loss (% of unchromed dyeing)		
Time of chroming, min. ...	15	30	45
Metomega Chrome Yellow ME ...	80	51	48
Metomega Chrome Orange ML ...	57	42	30
Metomega Chrome Brown RLL ...	18	14	10
Omega Chrome Black T	18	6	4
Omega Chrome Azurole B	22	14	10

This technique must of necessity be limited to dyes with good metachrome dyeing properties, although this need only be interpreted as including dyes which do not form insoluble chrome lakes in the dyebath. The range of such dyes is reasonably wide, both economically and from the point of view of fastness properties except with navies and blacks.

2. The Chromosol Mordant Process

This widens to an appreciable extent the range of dyes which can be dyed by a single-bath mordanting and dyeing method. It is of particular interest that included in the range are dyes of the Alizarine Blue OCR (*C.I.* 202) type, the basis of many economic navy blues.

Chromosol mordant is a complex sodium chromium oxalate. It gives an acid solution, and the dyeing is carried out under acid conditions. It may be anticipated, therefore, that fibre damage will not arise during the dyeing process. In order to determine whether this is so, wool yarn was treated under reflux at the boil with 3% Chromosol mordant for 1 hr. At the same time another sample of wool was treated in a similar manner with 3% of chromium fluoride. Tensile strength tests of single strands of the yarn compared with a sample of wool which had merely been wetted out in water gave the results in Table V.

Table V

Addition	Breaking Load (oz.)
None	13·03 ± 0·15
3% Chromosol mordant ...	12·22 ± 0·16
3% Chromium fluoride ...	12·92 ± 0·16

The decrease in tensile strength is therefore not as great as that given by an uncontrolled metachrome dyeing process.

The chief defect of the Chromosol mordant dyeing process is the slow rate of chrome lake formation compared with the metachrome process. Experiments were therefore carried out in order to see whether this could be rectified.

It was observed, while aftertreating dyeings of Omega Chrome Azurole B (*C.I.* 720) with 1% of chromium fluoride (calculated on the weight of material) that the dyeings were in general effect only partly developed, but throughout the wool some fibres were more completely developed than others. Since this might be due to the different degrees of damage in the fibre, a dyeing of Omega Chrome Azurole B was aftertreated at the boil with 1% chromium fluoride and 2% thioglycollic acid (calculated on the weight of material). Development of the true shade was much more complete than with chromium fluoride only, or with chromium fluoride and acetic acid.

The effect of an addition of thioglycollic acid (2% on the weight of material) was therefore examined, using dyes which can be applied by the Chromosol mordant dyeing process. In all cases the rate of development of the shade was increased, and was practically equal to the rate of development by the metachrome dyeing process.

At present the price of thioglycollic acid is too high to be of interest to the practical dyer, but this is due only to the lack of demand.

Attempts to replace thioglycollic acid by cheaper products were partly successful in that it was found that certain other acids and their sodium salts increased the rate of chrome lake formation with both Chromosol mordant and chromium fluoride, e.g. hydroxy-, monochloro-, and amino-acetic, lactic, salicylic, and oxalic acids (in amounts $< 1\%$). Their efficiency in increasing rate of chrome lake formation ranged in the same order as their effect on olation of chromium salts. None is as efficient as thioglycollic acid, which may be because the thiol group takes part in a secondary reaction as well as affects olation. Support is lent to this view by the fact that when a solution of thioglycollic acid is neutralised with alkali its efficiency becomes only of the same order as that of the sodium salts of other α-substituted carboxylic acids.

A similar increased rate of chrome lake formation with Chromosol mordant and chromium fluoride can be obtained by merely increasing the amount of mordant used. This would seem to indicate that only a part of the chromium salt in solution is able to take part in chrome lake formation. The nature of that part may well depend on the olation, but its exact nature will, for the present, remain only a speculation.

On experimental evidence from the laboratory the Chromosol mordant process may be used in exactly the same way as the metachrome process as far as the re-use of spent liquors is concerned. At the same time the extension of the range of dyes which may be used by this process is an additional advantage. In view of the saving in fuel and dyeing, the additional cost of the mordant may be of relative unimportance.

At this stage we have investigated two established dyeing methods, the metachrome process and the Chromosol mordant method, and have suggested how they may be of use in a scheme to apply fast dyes quickly and with economy of fuel. Economically, there may still be disadvantages, or it may be desired to use dyes which cannot be satisfactorily applied by either process.

3. Inactivation of Dichromate

An alternative method of single-bath mordant dyeing would be possible if the hot liquors containing dichromate from an afterchrome process could be treated in some way so as to convert the dichromate to a form which does not give rise to chrome lakes in the dyebath. The most probable conversion would be to a chromium salt.

As a preliminary, the use of chromium fluoride as an afterchroming agent was examined. A range of dyeings were prepared on wool yarn of chrome dyes in their acid-dyed state. The dyeings were divided into four parts, one part being kept in its unchromed form and the others being treated at the boil for 45 min. with 1, 2, and 4% chromium fluoride calculated on the weight of material. Degree of chrome lake formation was assessed as before. The results in Table VI were obtained.

Table VI

Dye	Colour Loss (% of unchromed dyeing)		
Chromium fluoride, %	1	2	4
Metomega Chrome Yellow ME ...	50	42	27
Metomega Chrome Green BLL ...	22	—	—
Metomega Chrome Brown RLL ...	10	10	8
Omega Chrome Black T	70	29	13
Omega Chrome Red B	74	30	18
Omega Chrome Green F	61	24	8

With the metachrome dyes chrome lake formation in the presence of only 2% chromium fluoride is as complete as with metachrome mordant. With dyes normally applied by the afterchrome process chrome lake formation is slower and less complete than by the afterchrome process, when none of the dyes used gave any measurable migration in a 1% solution of sodium carbonate.

Theoretically, sexivalent chromium may be converted into tervalent chromium in a number of ways, but many would not be suitable to dyehouse practice. In examining this problem, translation from laboratory to works may be more difficult because of the much greater bulk of liquor which must be dealt with. The process used must affect chromate only and not dye, otherwise undesirable decomposition products, inferior in both washing and light fastness, may be exhausted on to the wool. At the moment sodium nitrite appears to be the most economical product to use, but this view may be modified as a result of experience in using larger quantities of liquor.

Omega Chrome Black T is the most obvious dye to apply by this technique. With metachrome mordant 10% of dye produces only a grey shade. When the chromate is converted to tervalent chromium by means of nitrous acid, approx. 60% of the colour value is obtained. With the further addition of 2% thioglycollic acid this is increased to 80–90% colour value. A most satisfactory dyeing has been obtained by the addition of 3% sodium oxalate (calculated on the weight of material) to the dyebath. Raise to the boil, exhaust with acetic acid, and afterchrome in the normal way. The dyeing, on laboratory tests, appeared to have all the properties of an afterchrome dyeing carried out by normal methods.

At the moment, this is offered only as a laboratory experiment. It is intended to examine the technique on a larger scale and report upon it. In general, however, there does appear to be enough virtue in the technique to warrant further work upon it.

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Discussion

Dr. J. F. GAUNT: The danger of precipitation of dye when dyeing chrome dyes from a standing bath arises from the tervalent chromium and not from the sexivalent chromium present in the dyebath. It was shown by Carlene, Rowe, and Speakman [4] that appreciable amounts of tervalent chromium are present in spent dyebaths. The steps proposed by the lecturer for dealing with the residual chromium appear to be aimed at the sexivalent chromium. What effect does he consider the tervalent chromium will have?

Dr. LISTER: Our experience has been that it is not the tervalent chromium which causes precipitation of dye but oxidation by the sexivalent form. It may be, of course, that oxidation in the presence of tervalent chromium is more likely to lead to formation of a chromium complex than the presence of tervalent chromium alone. It appears to be possible to dye a greater number of dyes in the presence of a chromium salt than in the presence of a chromate or dichromate.

Dr. GAUNT: Many chrome dyes are susceptible to precipitation by even small concentrations of electrolyte. When using a standing bath as suggested by the lecturer, it is probable that a fairly high concentration of electrolyte will arise after two or three dyeings. Has this been investigated?

Dr. LISTER: It is true that the dye acids of many chrome dyes have poor solubility, and therefore salting out may take place with acids. Neutral salts, however, have not given rise to difficulties with the dyes we have tested, although there will doubtless be exceptions.

Mr. R. V. PERYMAN: The development of alkalinity in metachrome dyebaths is now becoming generally known, but there is still a good deal of uncertainty as to how much damage occurs to the wool through boiling in the metachrome dyebath at pH values in the region of 9. It has been stated that the wool is not damaged.

Recently a few experiments have been carried out to throw some light on the problem as follows—Three dyeings were run in the laboratory under conditions chosen to imitate as closely as possible commercial-scale metachrome dyeings carried to a deep shade. The dyeing formula was—

8%	...	Solochrome Brown MGR (ICI)
8%	...	Metachrome mordant
10%	...	Glauber's salt
6%	...	Ammonium sulphate (in addition to that contained in the metachrome mordant)

This was intended to approximate to extreme conditions used in commercial dyeing. A liquor : wool ratio of 18 : 1 was used, and escape of ammonia from the dyebath was prevented where necessary by fitting a reflux condenser. Purified flannel and calibrated wool fibres were boiled for 90 min. in this liquor, while the pH was controlled by the addition of ammonia. After washing the dyed wool in hot water and in running water overnight, it was then tested for loss in work required to stretch the single fibres, and in the case of the cloth its wet abrasion resistance and change in weight were measured.

The results are shown in the accompanying table.

Tests on Metachrome-dyed Fibres and Cloth

Dyeing	pH of Dyebath Range	pH of Dyebath Main Value	Loss in Work of Stretching Fibres 30% in Distilled Water (Mean %)	Wet Abrasion Resistance on Ring Wear Tester (rev.)	σ	Standard Error	Loss (% of A)	Change in Weight (%)
A	7·02–7·60	7·3	3·33	2069	179	60	—	+1·55
B	9·0–9·43	9·4	17·4	1113	139	36	46	+0·29 (−1·26 of A)
C	8·92–9·16	9·1	10·5	—	—	—	—	+0·56 (−1·0 of A)

Comparing the dyeing at pH 7·3 with the one at pH 9·4, it will be seen that a relatively large decrease has occurred in the work to stretch the alkaline-dyed fibres, and a decrease of 46% has occurred in the wet abrasion. This was accompanied by a relative loss in weight of 11%. The dyeing at pH 9·1 showed smaller but still significant losses.

Dr. LISTER: We much appreciate Mr. Peryman's contribution to this subject, and it is interesting that his results confirm our own. The chief answer to the question of fibre damage arising from the high pH values in metachrome dyeing is, of course, that high pH values are not an essential part of the metachrome process.

Mr. J. V. SUMMERSGILL: In view of the proposed use of thioglycollic acid, is the damage to wool serious under the suggested conditions of use?

Dr. LISTER: Thioglycollic is a standard reagent for the splitting of cystine cross-links in wool. In the presence of chromium, however, it is probable that the links are rebuilt through chromium, and no loss in fibre strength results. At the concentrations we are suggesting fibre damage is certainly negligible. As the conditions are acidic, damage is less than that obtained by treatment under normal metachrome dyeing conditions.

Mr. W. R. HEADING: (*a*) What are the mean values of the pH of dyeings in (i) orthodox metachrome dyeing and (ii) modified metachrome dyeing in which the mordant is added to the bath *after* the dye?

(*b*) What is the variation in pH during the course of the modified dyeing (ii) above?

(*c*) What is the best method of determining the *internal* hydroxyl ion concentration of the fibre during dyeing as distinct from the *external* hydroxyl ion concentration of the liquor?

Dr. LISTER: The actual pH of a metachrome dyeing carried out by the orthodox process will depend on the amount of alkali carried over from the scouring and the type of machine used.

Excluding winch dyeing, when the pH may fall to 7–7·5, under the best possible conditions the value may not exceed 8·5; on the other hand, values of 9·5–10 are by no means uncommon.

When the mordant is added after the dye, lower pH values will always be obtained, firstly because of the shorter time of contact between fibre and chromium, and secondly because in many cases a small addition of acid may be required (of the order of 0·5% acetic acid). Under the worst conditions the pH at the end of the dyeing should not exceed 8·5. If the other precautions mentioned are taken, then the pH by both methods will not exceed 7. The main object of the modified process is not to control pH but to obtain more level dyeing.

There appears to be no satisfactory method of determining the internal pH of wool. It has been suggested that this may be done by immersing standard weights of the material in varying quantities of distilled water. After plotting pH against volume of water, the graph is extrapolated to give the pH in a volume equal to the moisture of conditioning.

In the absence of dye it is possible to calculate the internal pH from an equation based on the Donnan theory of membrane equilibria [6].

COMMUNICATIONS

The Rôle of Foam in Detergent Action

D. G. Stevenson

Foams have the power of sucking oil into the junctions between the liquid films or lamellæ which separate air bubbles, probably because the curvature of the water–air surface is greatest, and the pressure in the liquid lowest, at these junctions. When a foam carrying lines of oil along these junctions breaks, the oil is dispersed as fine droplets; therefore foams can assist emulsification of oil.

INTRODUCTION

The cleansing action of soaps, and of all detergents except organic solvents, requires first that the grease or other dirt shall be detached from the solid surface to be cleaned, second that the dirt shall not be redeposited on the solid. Practically all water-soluble detergents are excellent wetting agents, and most of them tend to stabilise suspensions or emulsions of dirt, which usually has a rather hydrophobic surface in the absence of a detergent. More interest attaches to the mechanism by which dirt is detached from a solid surface. Adam [1] showed that solutions of detergents with a soap-like constitution, long aliphatic chains with electrolytically dissociated end-groups, roll up layers of oil, thinly spread on the surface of textile fibres, into small globules easily shaken off the fibres. This is done through adsorption of a film, possibly unimolecular, of the detergent on the solid surface, which alters the contact angle formed by the water–oil surface with the fibre, from zero in the oil and 180° in water to zero in the detergent solution and 180° in the oil. This action has been confirmed by Kling, Langer, and Haussner [2]; it does not depend on the presence of foam.

The great majority of aqueous detergent solutions foam easily, but precisely what function the foam or lather performs in removing dirt still appears unknown. Bikerman [3] writes that "the part played by foam gets marks ranging from 'essential' to 'non-existent' . . . ". Chwala [4] suggests that particles of solid dirt such as soot, made hydrophilic by the detergent, are drawn into the liquid films separating air bubbles in the foam; this view appears to be supported by Reumuth [5]. Niven [6] attempts to draw an analogy between the froth-flotation process for separating minerals and any power a foam may have to carry dirt; but any such analogy must be at best very superficial, since the action of collectors, which cause some minerals to adhere to an air–water surface, is well known to be due to their rendering the mineral surface strongly *hydrophobic*, whereas practically all detergents render surfaces, on which they are adsorbed, more *hydrophilic*.

It seems certain that detergent action can be efficient when foaming power is small: Sisley [7] points out that, when the foam on a soap solution is much reduced or destroyed by addition of anti-foaming agents such as tributyl phosphate, the detergent action remains practically unimpaired. Conversely, solutions of saponin, which foam extremely well, have little detergent power. Foaming power and detergent action are both consequences of the surface activity of detergents, the former caused by the adsorption of the detergent at the air–water surface, the latter by adsorption at the surface between the solid and the water. In the case of soap, as generally used domestically, the appearance of a permanent lather is a reliable indication that the solution is fit for washing, because it shows that some soap is present in the solution in excess of the amount which is wasted by precipitation as calcium or other insoluble soaps in moderately hard water; it is no proof that the lather is essential for removing the dirt.

In this paper the action of foams of soap and other detergents on oil smeared on solid surfaces, usually glass, is studied; it is shown that the oil is drawn into the thin liquid lamellæ separating the air bubbles, concentrating at the linear junctions where two or more lamellæ join. This is probably due to the air–liquid surface being most strongly curved at these junctions, with a consequent reduction of pressure in the liquid at these lines. The oil is detached from the glass by the contact angle effect mentioned at the beginning of this paper, and then sucked into the interlamellar junctions, where the pressure is a minimum. The photographs show the various stages of this

process and the mechanism of removal of the oil by foam.

EXPERIMENTAL

As oil the colloidal suspension of graphite in mineral oil known as Oildag (Acheson) was used; the graphite in this is so finely divided that it may, for the present purpose, be considered simply as imparting a very intense colour to the oil. The oil was painted on glass slides, or as a ring on the interior of glass tubes in the experiments on flowing foams. Four solutions were used—sodium oleate, a secondary alkyl sulphate, a detergent of the non-ionic polyoxyethylene type, and cetyltrimethylammonium bromide (CTAB), a cationic paraffin-chain salt with little detergent power. All solutions used were of approx. 0·2% concentration, calculated on the active agent present in the commercial preparations.

RESULTS AND DISCUSSION

Fig. 1–4 show the effect of a fine foam made from 0·2% alkyl sulphate solution by blowing air through a sintered glass disc (porosity 2) at the bottom of the vessel containing the solution. The smear was on the underside of a glass slide placed on top of this vessel, and the foam reached the smear from below; the photographs were taken from above by reflected light from a lamp above the glass. They show the state of the oil in immediate contact with the glass. After a few seconds' contact with foam, whitish patches appear in the oil; these quickly develop into more or less circular areas, most of which (though not quite all) are free from oil. At the same time, the oil spreads far beyond the original boundaries of the smear, appearing as thin lines where the thin liquid lamellæ between air bubbles meet the glass. Even after three minutes the oil continued to spread in these thin lines, beyond the field of view.

Fig. 5–7 show how some of the oil is removed from the glass altogether, along the junctions between lamellæ; Fig. 7 shows a black four-ray star where four such lines meet. A much coarser foam was used to obtain these photographs, to avoid confusion from too many lines and excessive reflection from the liquid–air surfaces.

Foams of sodium oleate and of the non-ionic detergent broke up an oil smear in a similar manner, the action of the non-ionic detergent being rather slower than that of the other two.

Cetyltrimethylammonium bromide, which has little detergent action, sucks some of the oil into the junctions between lamellæ and glass, but does not remove the oil from the glass; Fig. 8 shows all the oil in the lamellæ with an alkyl sulphate foam, but a good deal remains smeared on the glass with a CTAB foam (Fig. 9). The reason for this difference is that sodium oleate and the alkyl sulphate reduce the contact angle in the water between the oil–water surface and the glass to zero, in a minute or less, causing the glass to be wetted by water instead of by oil. CTAB scarcely reduces this angle at all, to only 150° as a minimum in the concentration employed; this is insufficiently low to facilitate removal of oil from glass.

Frequently, and particularly when the foams break as bubbles burst, the thin lines of oil break up into small globules. In Fig. 10 there is partial break-up; in Fig. 11 a few small globules have become completely detached. This disintegration of the oil into tiny globules may assist emulsification of the oil. Very small droplets such as those shown in Fig. 11 have been observed to fall freely, under gravity, down interlamellar junctions, larger masses being held at the intersections with tentacles extending along several lamellæ.

If a foam is allowed to drain, by keeping it for some time well above the parent solution, the lamellæ become thinner and the curvature at their junctions more pronounced. This helps to spread the oil: Fig. 12 shows the original smear on a vertical glass surface, and Fig. 13 the action of a foam which becomes progressively better drained higher up the surface. The oil is spread in the upper part to a greater width than in the lower part. In the solution below the foam, the oil is rolled up into globules, as described in the first paragraph of this paper.

Fig. 14 shows the process by which oil is sucked into the lamellæ. A foam was formed in a rectangular glass cell, and a drop of oil allowed to run down the side of the cell nearest the camera. Photographs taken at intervals of one second show that, when the oil drop reaches the lamella, it suddenly elongates on one side and is sucked in, soon finding its way to the junction between three lamellæ. It appears as if the oil drop begins to elongate just before it touches the lamella; this is almost certainly an optical illusion, as the lamella is curved round where it wets the glass and has a slightly greater thickness here than appears in the photograph. The process of sucking the oil into its final position is practically complete in four seconds.

Fig. 15–17 show the action of a slowly moving alkyl sulphate foam on a ring of oil painted inside a horizontal tube, the initial position (Fig. 15) being marked by a strip of white paper with a black line on it, on the outside of the tube. Fig. 18 shows the effect of a slowly moving alkyl sulphate solution without foam: the oil rolls up into globules, which later rise to the upper side of the tube, and then roll slowly along with the moving solution. Fig. 19 and 20 show the action of a moving sodium oleate foam, which also quickly removes all the oil from the glass. By contrast, CTAB (Fig. 21 and 22) merely spreads the oil a little way along the glass.

It is concluded from the above experiments that foam may play a very definite part in the removal of oils and fats from smooth surfaces, such as are met with in dishwashing. However, it is unlikely that foam will aid significantly the removal of soil in laundering: although some air bubbles may pass through the interyarn spaces in a fabric during washing, none is likely to pass through the interfibre spaces where the soil is more firmly held, as any pressure difference across the fabric will be released through the wider interyarn spaces.

* * *

Fig. 1— Oil Patch before Contact with Foam

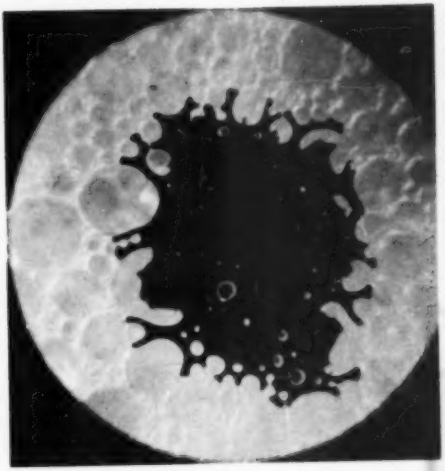

Fig. 2— After 15 sec. Contact

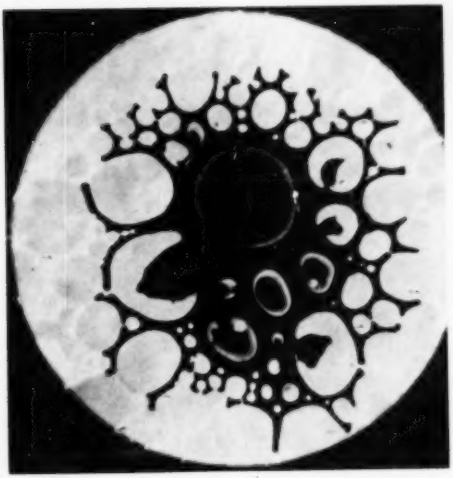

Fig. 3— After 45 sec.

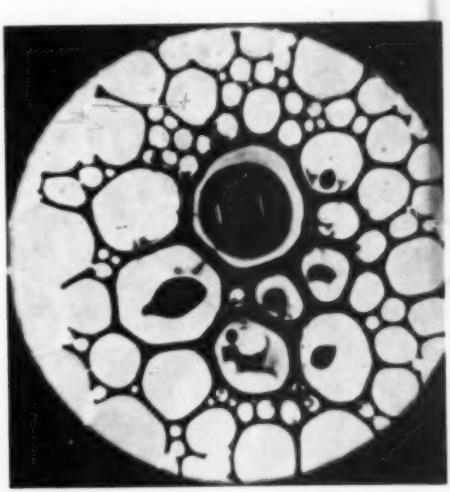

Fig. 4— After 3 min.

Fig. 1–4— Action of Fine Foam (Alkyl Sulphate) on Oil Patch (× 8)

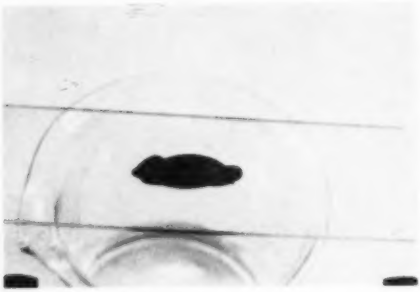

FIG. 5.—Before Contact

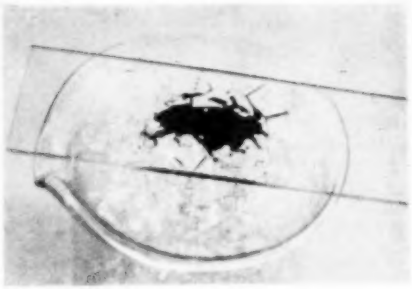

FIG. 6.—After 1 min.

FIG. 7.—Oil in Lamellar Junctions of Foam

FIG. 5-7.—Action of Coarse Foam (Alkyl Sulphate) on Oil Patch

FIG. 8.—Oil completely sucked off Glass (Alkyl Sulphate Foam) (× 16)

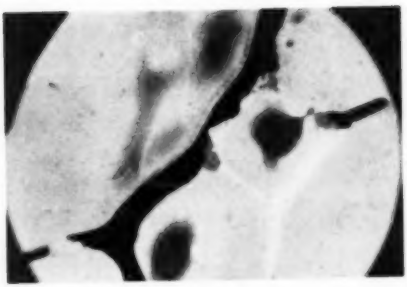

FIG. 9.—Oil partly sucked off Glass (cTAB Foam) (× 16)

FIG. 10— Partial Breakup into Tiny Globules

FIG. 11— Some Fine Globules

FIG. 10 and 11— Sodium Oleate Foam (× 16)

FIG. 12— Before Contact

FIG. 13— After Contact

FIG. 12 and 13— Action of Foam on Vertical Oil Smear

FIG. 14— Sucking of Oil Drop into Foam Lamella

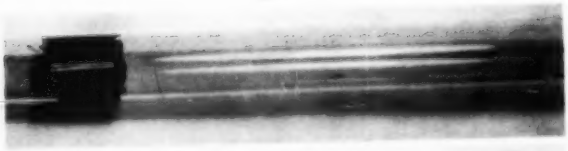

Fig. 15 — Before Exposure

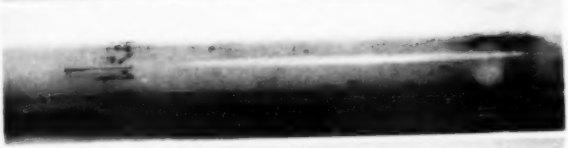

Fig. 16— After 2 min.

Fig. 17 — After 10 min.

Fig. 15-17 — Action of Alkyl Sulphate Foam moving at 3 cm./min. on Oil Ring in Horizontal Tube

Fig. 18 — After 3 min. in Moving Alkyl Sulphate Solution (without Foam

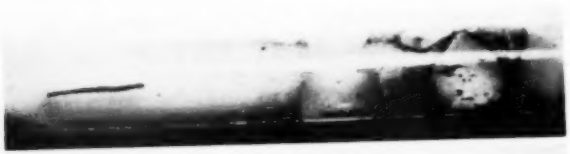

Fig. 19— After 2 min.

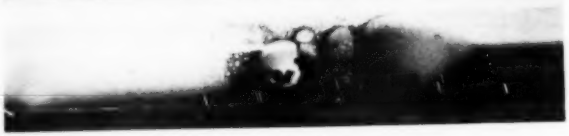

Fig. 20— After 10 min.

Fig. 19 and 20 — Action of Moving Sodium Oleate Foam

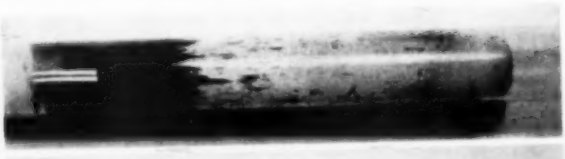

Fig. 21 — After 2 min.

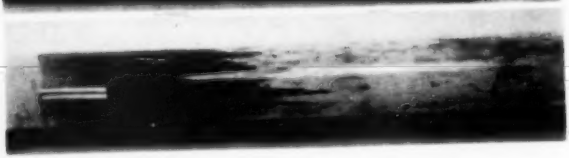

Fig. 22— After 10 min.

Fig. 21 and 22 — Action of Moving CTAB Foam

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The Heats and Free Energies of Formation of some Hydrogen Bonds

M. ST. C. FLETT

The free energies and heats and entropies of formation of hydrogen bonds between several pairs of compounds in carbon tetrachloride solution have been calculated from infrared spectra. Efforts have been made to correlate the strengths of some of these bonds with dyeing phenomena. Interpretations are suggested for the variations in the strengths of bonds in terms of electronic shifts in the participating molecules. Correlation of the frequency shifts and changes in intensity of the bands which accompany hydrogen bond formation with the strengths of the bonds formed is also attempted.

It has been suggested [1] that hydrogen bonds may play an important part in attaching dyes to fibres, but few quantitative data on the strengths of the hydrogen bonds postulated are available with which to test this hypothesis. Accordingly infrared spectroscopic measurements are in progress to supply these data. Although firm conclusions about the dyeing problem cannot yet be drawn, it is felt that the results on hydrogen bond strengths so far obtained are of sufficient interest to be reported.

There are obvious difficulties in measuring directly by spectroscopic methods the strength of a hydrogen bond between a fibre and a dye molecule attached to it. Quantitative measures of the heats of formation of bonds could be obtained only by measuring the difference between the frequency of some band associated with a dye molecule on the fibre and in an inert medium, and applying some such rule as that of Badger [2]. Also some important fibres absorb so strongly that it would not be possible to study the characteristic bands of many dyes.

Accordingly pairs of model compounds were selected one of which contained a chemical group occurring in fibres and the other a group occurring in some class of dye. One component X–H carried a hydroxyl OH or secondary amino –NH– group, and the other component Y a group, such as C:O, C:N, N:N, or –O–, with which the X–H group might form a hydrogen bond. Such pairs of compounds were studied in carbon tetrachloride solution. By measuring spectroscopically the change in intensity of a band associated with the X–H molecule, attempts were made to determine the equilibrium constants between the molecules and hence to deduce free energies of formation of bonds. The temperature dependence of the free energies was used to estimate the heats of formation of the bonds.

EXPERIMENTAL

The chemicals used were in all cases purified before use by fractional distillation or recrystallisation, only materials which showed the accepted melting or boiling points being used. The solvent was AnalaR carbon tetrachloride, which was dried by bubbling through it a stream of air dried over calcium chloride and phosphorus pentoxide, as described by Fox and Martin [3].

All solutions were made up by weight so that the mole fractions of the components could be calculated. It is well known that hydroxyl compounds and amides readily undergo self-association in solution [4]. This was guarded against by using such compounds at concentrations (< 0·01 M.) at which self-association was negligible. In such cases, in order to move the equilibrium—

$$XH + Y \rightleftharpoons XH...Y$$

to the right to a conveniently measurable extent, it was necessary to use considerably higher concentrations of the Y components (about 0·1 M.).

The N–H and –OH links have highly characteristic bands between 2·7 and 3·0 μ. In the present work, as in most previous spectroscopic studies of the hydrogen bond, these bands were used. The spectra of the solutions were therefore determined from 2·5 to 3·3 μ. A Hilger D 209 spectrometer with lithium fluoride and calcium fluoride prisms was used. They were calibrated in wave-numbers in the usual way, using the known values of the bands of phenol and benzyl alcohol solutions and gaseous ammonia, carbon dioxide, and water vapour. Since accurate optical density measurements were essential, it proved more satisfactory to plot the spectra by point-by-point measurement of galvanometer deflections than from automatic records. To obtain galvanometer deflections large enough to be accurately measurable, it was necessary to use slits rather wider (0·1 mm.) than is customary in this spectral range. Absorption by the Y component, which was in any case not very intense in this spectral region, was as far as possible allowed for by placing in the blank cell, instead of pure carbon tetrachloride, a solution of Y at the same concentration as in the mixture.

The absorption cells were of brass with fluorite windows, since this combination is suitable for work at elevated temperatures, on account of the

similar coefficients of expansion of the materials [5]. They were mounted in a small electrically heated air thermostat which could be slid to and fro so as to put the solution and blank cells alternatively into the light beam. The temperature inside each cell was measured thermoelectrically and could be controlled to ±0·5°c. Spectra were measured at room temperature and 60°c. The cells were fitted to small water-cooled condensers to prevent loss of solvent by evaporation at the higher temperature.

RESULTS AND CALCULATIONS

Suppose that a hydrogen bonding process—

$$\underset{1\ \text{mol.}}{XH} + \underset{1\ \text{mol.}}{Y} \rightarrow \underset{1\ \text{mol.}}{XH...Y}$$

takes place at constant temperature and pressure. If, as seems reasonable to assume in dealing with fairly dilute solutions, activities can be set equal to mole fractions, the change of Gibbs free energy associated with the hydrogen bonding process is given by—

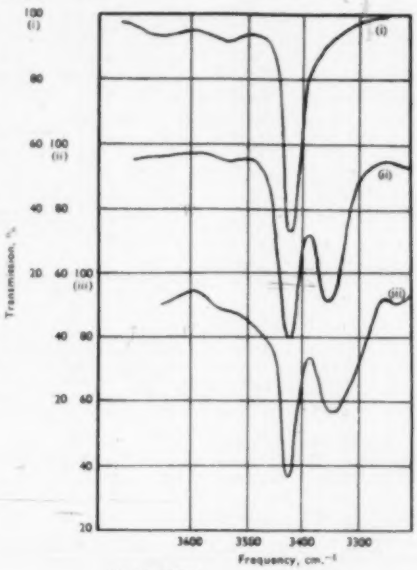
$$\Delta G = -RT \ln \frac{x_{XH...Y}}{x_{XH}\, x_Y} = -RT \ln K$$

the xs being mole fractions and the K an equilibrium constant. Also the heat of formation is given by—

$$\Delta H = -RT^2 \frac{d \ln K}{dT}$$

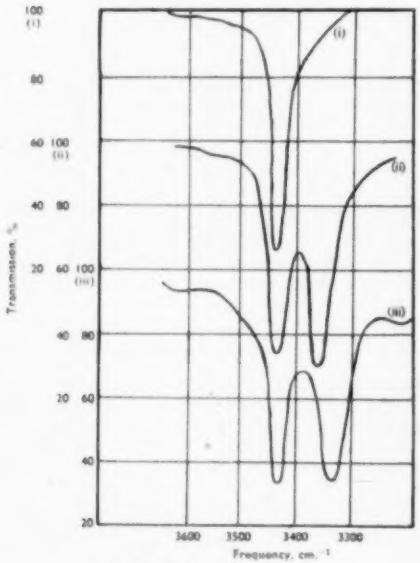
or, if ΔH is independent of temperature—

$$\Delta H = \frac{R \ln K_1/K_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$



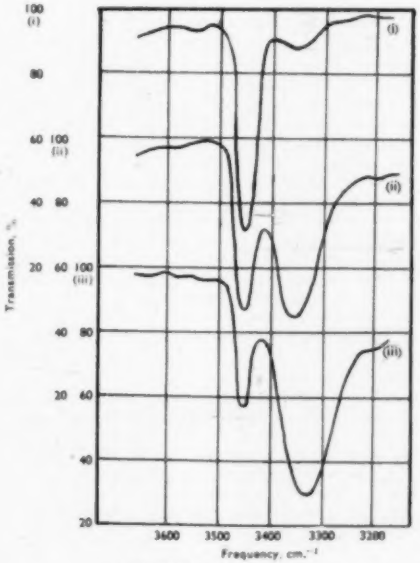
(i) No addition
(ii) + Dioxan (0·581 M.)
(iii) + Dimethylformamide (0·1272 M.)

FIG. 2.—Diphenylamine (0·0113 M.) at 60°c. (cell 1 cm.)



(i) No addition
(ii) + Dioxan (0·607 M.)
(iii) + Dimethylformamide (0·1332 M.)

FIG. 1.—Diphenylamine (0·0118 M.) at Room Temperature (cell 1 cm.)



(i) No addition
(ii) + Dioxan (0·600 M.)
(iii) + Dimethylformamide (0·1224 M.)

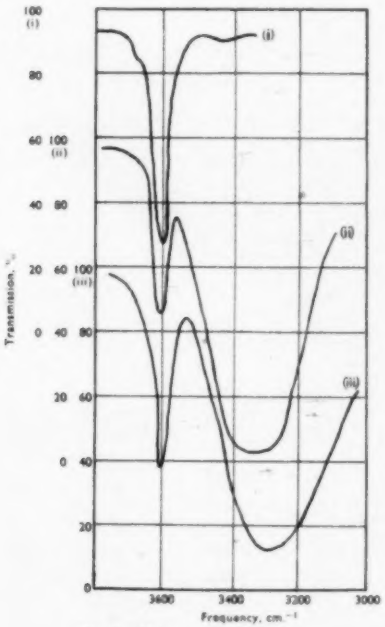
FIG. 3.—p-Benzotoluidide (0·00945 M.) at Room Temperature (cell 1 cm.)

The first step in the calculation is the evaluation of K from the spectra. Examination of Fig. 1–5 shows only a single strong band in the spectra of the X–H components (benzyl alcohol, phenol, *p*-benzotoluidide, and diphenylamine), due to the X–H stretching vibrations. The broad band indicating dimer formation is just apparent in the spectra of benzyl alcohol, phenol, and *p*-benzotoluidide. As a second component Y is added, a second band develops, associated with the modified X–H stretching vibrations in the complex, while the original X–H band becomes weaker.

Suppose an X–H solution containing C moles per litre has an extinction coefficient ε. If, then, in some mixture of X–H with Y the extinction coefficient at the X–H band is ε', the concentration of unbonded X–H is $C\varepsilon'/\varepsilon$. If also there were initially a moles of X–H and b moles of Y in the mixture, the equilibrium concentration of the complex is $a-C\varepsilon'/\varepsilon$, and that of Y is $b-a+C\varepsilon'/\varepsilon$. The equilibrium constant is therefore—

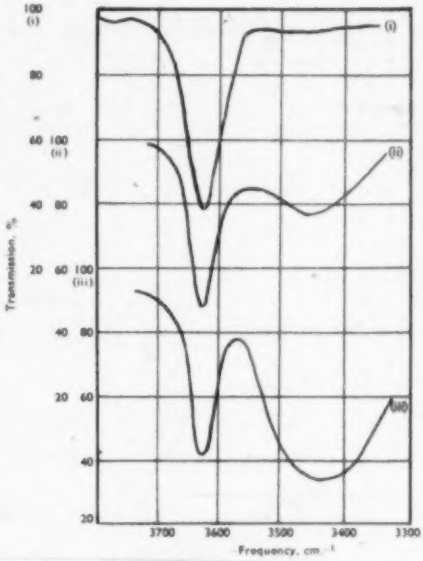
$$K = \frac{a - \frac{C\varepsilon'}{\varepsilon}}{\frac{C\varepsilon'}{\varepsilon}\left(b - a + \frac{C\varepsilon'}{\varepsilon}\right)} \times N$$

N being the total number of moles, including those of the solvent, carbon tetrachloride. In the case of dioxan, which has two functional groups, the molar concentration of ether groups rather than of molecules was taken. This analysis assumes that



(i) No addition
(ii) + Dioxan (0·2600 M.)
(iii) + Dimethylformamide (0·0125 M.)

FIG. 4.—Phenol (0·00481 M.) at Room Temperature (cell 3 cm.)



(i) No addition
(ii) + Azobenzene (0·492 M.)
(iii) + Dimethylformamide (0·0625 M.)

FIG. 5.—Benzyl Alcohol (0·00452 M.) at Room Temperature (cell 3 cm.)

only complexes of the type X–H...Y are formed and that the Y molecules do not self-associate. The main source of error in the procedure lies in the evaluation of ε', since overlap by the complex band has to be corrected for, and in the cases where the amount of complex formed is small, the correction has a large effect on the result. The present results were obtained by correcting graphically for the overlap, and the absence of a steady variation in the calculated values of the equilibrium constant with increasing concentration of the solutions suggests that the method is fairly satisfactory. It was not possible, however, to obtain quantitative results in systems such as benzyl alcohol with anisole and with benzoquinone owing to excessive overlap.

The results are given in Tables I and II. Table I gives the constants calculated from various mixtures and the differences between the wavenumbers of the absorption bands of the hydrogen-bonded groups and the unbonded groups which occur at 3620 cm.$^{-1}$ for benzyl alcohol, 3615 cm.$^{-1}$ for phenol, 3450 cm.$^{-1}$ for *p*-benzotoluidide, and 3430 cm.$^{-1}$ for diphenylamine. The molecular extinction coefficients of the "complex" band are also included, and may be compared with the corresponding values for the unassociated molecules, which are included in parentheses after each extinction coefficient value. They were calculated from the equation—

$$\varepsilon = \frac{1}{Cl} \ln \frac{I_0}{I}$$

where C = concn. of soln. in moles/litre and l is

TABLE I

Equilibrium Constants, Frequency Shifts, and Band Intensities

Components X–H	Components Y	Type of Hydrogen Bond	Initial Concn. (moles/litre) X–H	Initial Concn. (moles/litre) Y	Room Temp. (° C.)	Equilibrium Constant K_t	Equilibrium Constant K_∞	Frequency Shift (cm.$^{-1}$) $\Delta\nu_t$	Frequency Shift (cm.$^{-1}$) $\Delta\nu_\infty$	Extinction Coeff. ϵ_t	Extinction Coeff. ϵ_∞
Diphenylamine	Dioxan	>N–H···O<	0·011676	1·2464	22	5·52	2·65	77	70	122·1 (49·2)	106·5 (42·6)
			0·012805	0·6012	22	3·96	2·73				
			0·011840	1·1720	22·5	5·58	3·22				
			0·011700	0·5888	21·5	3·82	2·48				
			0·011880	0·3352	21	3·96	3·31				
	Dimethylformamide	>N–H···O=C< (?)	0·011820	0·13328	21	39·3	18·5	90	85	150·3 (49·2)	150·3 (42·6)
			0·011748	0·29772	20·5	41·2	20·1				
			0·011884	0·14934	20·5	32·8	15·8				
	Benzyl acetate	>N–H···O=C< (?)	0·011888	0·34200	20	13·3	—	45	45	—	—
			0·012032	0·70052	24	16·6	7·8				
			0·011840	0·4802	20	9·9	—				
p-Benzotoluidide	Dioxan	>N–H···O<	0·009276	1·124	21	8·57	5·16	100	95	71·1 (48·6)	57·3 (45·6)
			0·009724	0·6089	21·5	6·28	3·91				
			0·009372	0·8284	23	7·02	4·96				
	Dimethylformamide	>N–H···O=C< (?)	0·009676	0·12264	22	136	66	120	120	78·6 (48·6)	62·6 (45·6)
			0·009428	0·2636	23	141	67				
			0·009800	0·08976	21·5	113	72				
	Benzyl acetate	>N–H···O=C< (?)	0·009424	0·33014	24	(26·7)	(12·2)	70	60	—	—
Phenol	Dioxan	–O–H···O<	0·004832	0·2990	23·5	19·8	7·9	270	260	—	250
			0·004788	0·52508	24·8	21·0	7·8				
	Dimethylformamide	–O–H···O=C< (?)	0·004896	0·03040	23·5	461	151	335	330	212 (38·3)	180 (36·0)
			0·004876	0·02100	23·8	381	113				
			0·004844	0·02252	24·5	440	—				
	Benzyl acetate	–O–H···O=C< (?)	0·005404	0·012012	21·5	53·2	28·9	180	165	—	—
			0·005380	0·013032	21·0	43·5	20·3				
	Acetonitrile	–O–H···N≡C–	0·005412	0·21888	23	31·8	13·6	—	150	—	—
			0·005380	0·10956	22	23·2	11·0				
Benzyl alcohol	Azobenzene	–O–H···N=N–	0·004600	0·24528	23·2	7·10	2·80	175	165	33·2 (27·0)	—
			0·005642	0·2950	23	4·80	—				
			0·004584	0·4924	25·3	6·20	3·00				
			0·005642	0·4940	23·0	5·06	1·90				
			0·004792	0·7244	23·5	5·09	2·75				
	Dimethylformamide	–O–H···O=C<	0·004580	0·09212	24·6	59·4	28·9	185	175	104 (30·5)	101 (26·9)
			0·004592	0·12248	24·4	71·5	34·1				
			0·004608	0·24716	22·2	71·5	24·2				
	Acetonitrile	–O–H···N≡C–	0·004756	0·4336	22·8	—	—	80	—	—	—
	Anisole	–O–H···O<	0·00570	0·466	20–23	—	—	85	—	—	—
	p-Benzoquinone	–O–H···O=C<	0·00578	0·184	20–23	—	—	70	—	—	—
Methylaniline	Dimethylformamide	>N–H···O=C< (?)	0·354	0·269	20–23	—	—	60	—	—	—
	Dioxan	>N–H···O<	0·379	0·461	20–23*	—	—	55	—	—	—
	Benzyl acetate	>N–H···O=C< (?)	0·320	0·690	20–23	—	—	30	—	—	—
Aniline	•Dimethylformamide	(?)	0·442	0·245	—	—	—	20	—	—	—
	•Ethyl ether	(?)	0·555	0·778	—	—	—	< 10	—	—	—
	•Ethyl acetate	(?)	0·535	0·532	—	—	—	< 10	—	—	—

* These figures refer to both the symmetric and anti-symmetric vibration modes.

TABLE II

Thermodynamic Data of Hydrogen-bonding

Components X–H	Components Y	$-\Delta G_t$	$-\Delta G_\infty$ (g.cal./mole)	$-\Delta H$	$-\Delta S$ (g.cal./°c./mole)	$\Delta\nu$ (mean) (cm.$^{-1}$)
Accuracy, "p"		±3	±5	±19	±50	—
Diphenylamine	Dioxan	890	700	2300	5	72
	Dimethylformamide	2120	1920	3600	5	87
p-Benzotoluidide	Dioxan	1160	1020	2300	4	97
	Dimethylformamide	2850	2750	3800	3	120
Phenol	Dioxan	1780	1360	5500	11	265
	Dimethylformamide	3570	3230	6400	9	332
	Benzyl acetate	2270	2120	3300	4	177
	Acetonitrile	1980	1660	4200	7	160
Benzyl alcohol	Azobenzene	1020	690	3700	9	170
	Dimethylformamide	2480	2230	4500	7	180

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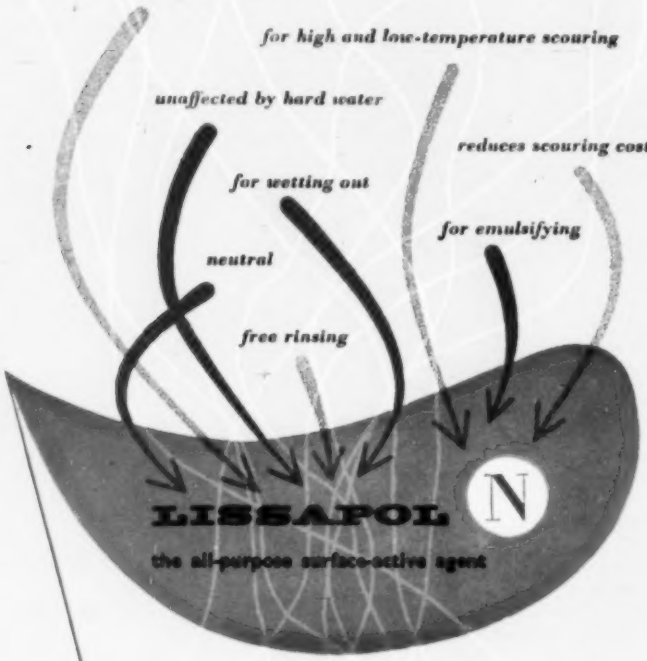

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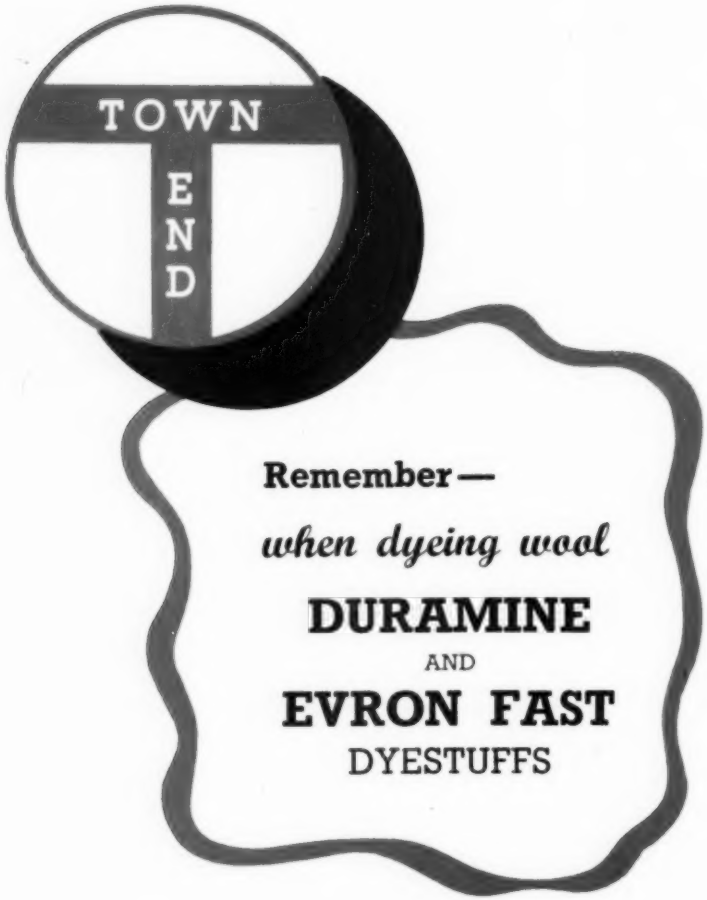

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the cell thickness in cm. Table II lists the values of the changes in free energy, heat content, and entropy involved. High accuracy cannot be claimed for the values. As seen from Table I, unavoidable experimental errors and approximations on which the theoretical analysis is based cause the "constants" for a given system to vary somewhat. The average standard errors of the mean changes in free energy at room temperature and 60°c., heat content, and entropy are respectively 3, 5, 19, and 50%. The figures do, however, give at least a semi-quantitative picture of the bonding process.

DISCUSSION

If a dye is able to form hydrogen bonds with active groups in fibres, it is likely also to be able to form bonds with water in a dyebath. Also the chains of cellulose and polyamides are known to form internal and intermolecular hydrogen bonds. Accordingly the overall dyeing process may involve rupture and formation of various such bonds. The present measurements cannot therefore be expected to be capable of direct correlation with the heats of dyeing. With this in mind it is intended to extend them by measurements on some of the possible dye–water and fibre–water bonds. It is possible, however, to see in which dye–fibre systems hydrogen bonding is most likely to be important. The strong bond observed between an azo and a hydroxyl group is in agreement with the hypothesis[1] that such bonds are important in attaching azo dyes to cellulose. The comparative weakness of the bonds involving the ether link indicates that the ether groups in cellulose may not be involved in dye attachment. This agrees with observations[6] on the combination of direct dyes with soluble polymers.

The amide C:O group forms strong bonds with the –NH– group, with the aliphatic hydroxyl group, and particularly with the phenolic hydroxyl group. Hydrogen bonding may therefore be a factor in attaching dyes containing amino, peptide, and phenolic groups to peptide groups in fibres. The fairly weak bonds involving the acetate group suggest that in cellulose acetate the residual hydroxyl groups may be important in dye attachment.

The results also throw some light on the problem of hydrogen bonding more generally. Much quantitative work has been done on the self-association of alcohols and phenols[4], amides[7], and carboxylic acids[5]. Although many qualitative studies have been made[8], few quantitative measurements of the strengths of hydrogen bonds between unlike molecules have been undertaken, as indicated in a recent review article[9]. In most of the work of Gordy and his co-workers[8] a compound X–H was dissolved in various solvents, and the X–H frequency determined in each at one temperature. Apart from doubt about the relation between frequency shift and strength of a bond as measured by its heat of formation, it appears that the changes in dielectric constant from solvent to solvent may affect frequency shifts so measured. The present technique has the advantage that no large changes of dielectric constant can occur, and that free energies and heats of formation are measured more directly.

In all cases the heats of formation are numerically greater than the free energies. The entropy change for the process—

$$X{-}H + Y \rightarrow X{-}H\ldots Y$$

is therefore always negative, which is to be expected from the increased restriction of motion of the molecules. A relationship between heat and entropy changes might also have been expected, but none emerges clearly from the data, probably because of inaccuracies, though there is a slight tendency for large heats and entropies to occur together.

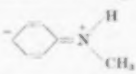
For a given X–H link, the numerical values of $\Delta\nu$ and ΔH tend to increase together, but the heats are not sufficiently accurate for the nature of the dependence to be apparent.

The frequency shifts $\Delta\nu$ are not greatly affected by temperature. The intensity of an X–H band, as measured by its peak extinction coefficient, is always increased by hydrogen bonding. The proportional increases vary widely, however, from bond to bond, between the extreme values of 1·2-fold increase for the system benzyl alcohol–azobenzene to 7-fold for phenol–dioxan. Changes in shape of the "bonded" band may account for some of these variations.

There are appreciable changes in extinction coefficients over the temperature range considered. The coefficients of monomeric phenol, benzyl alcohol, *p*-benzotoluidide, and diphenylamine fall by 5–15% from 20 to 60°c. (Table I), and on the whole the strengths of the "complex" bands also fall slightly with increasing temperature.

The relative strengths of the hydrogen bonds formed by the various X–H compounds considered in the present work seem on the whole to be in accord with the concepts of the electronic theory of chemistry.

If it is supposed that the hydrogen bond is predominantly electrostatic in character, as is strongly suggested by the calculations of Coggeshall[10] and Davies[11], then in a bond X–H…N or X–H…O, since the nitrogen or oxygen atom will have a slight negative charge, the bond strength will increase with the positive charge on the hydrogen atom. This is in accordance with the fact that both the ΔH and $\Delta\nu$ values suggest that O–H links form stronger bonds than N–H links. The oxygen atom, being more powerfully electron-attracting, will leave the hydrogen more positive. This is also suggested by the stronger acidity of OH compounds. A somewhat similar argument may account for the increase in hydrogen bond strengths in the series methylaniline, diphenylamine, and *p*-benzotoluidide. The nitrogen atom in methylaniline will donate electrons to the aromatic nucleus by an electronic shift, which may be regarded as resonance involving such forms as—



It will therefore recover some of the electron density so lost by attracting electrons from the

N–H link, leaving the hydrogen atom more positive than in a simple amine. The process will be carried further in diphenylamine with two aromatic nuclei, suggesting a reason why the latter forms stronger hydrogen bonds. In *p*-benzotoluidide, the nitrogen atom may give up electrons to the powerfully electron-attracting oxygen atom

(resonance with O⁻—C=N⁺—H), again in turn depleting the hydrogen atom, and rendering it capable of forming strong hydrogen bonds. The greater strength of the bonds involving phenol than those involving benzyl alcohol may be similarly explained. The oxygen atom of phenol will lose electrons to the ring by an electromeric shift, and in turn will draw electron density from the hydrogen atom, leaving it more positive than in benzyl alcohol, where this phenomenon cannot occur.

* * *

The measurements on the systems phenol–dioxan, phenol–dimethylformamide, and benzyl alcohol–azobenzene were made by Mr. M. J. Khan, Oxford University, during his Summer Vacation 1950. I am indebted to I.C.I. (Nobel Division) for the loan of a lithium fluoride prism with which some of the measurements were made, and to several colleagues for useful discussions and suggestions, particularly to Dr. T. Vickerstaff and Dr. R. H. Peters, who originally suggested the problem.

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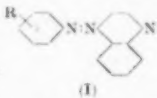
Some Further Investigations into the Fading Rates of Monoazo Dyes

E. ATHERTON and R. H. PETERS

The fading rates of a series of simple monoazo dyes have been investigated with a view to assessing the effect of substituent groups on light fastness. Work reported previously has been checked and extended by the inclusion of dyes with electrophilic substituent groups. The linear relation between destruction efficiency and the Hammett σ value for the substituent group previously reported has been found to be slightly in error and has been modified accordingly. Possible reaction mechanisms are discussed.

In 1949 Atherton and Seltzer [1] reported measurements of the rate of fading of substituted phenylazo-α-naphthylamines (I) in cellulose acetate films.



(I)

The films, which were cast from an acetone solution of cellulose acetate and dye in order to ensure uniformity, were exposed to the radiation from a high-intensity carbon arc. The amount of dye destroyed was estimated spectrophotometrically, and the amount of light falling on the film during each exposure was measured by means of a light flux integrator; by combining the latter quantity with the absorption characteristics of the dye and the spectral energy distribution of the light from the arc, they were able to calculate the total amount of energy which the dye had absorbed during the fading reaction. They used, as a measure of the fading rate, the initial slope of the graph obtained by plotting the amount of dye destroyed against the energy absorbed; this was defined as the destruction efficiency k. Plotting the logarithm of the ratio of the destruction efficiencies of the substituted and the unsubstituted compound (I, R = R and R = H) against Hammett's σ value for the substituent R, a straight line was obtained, those dyes with positive σ values having the higher light fastness.

The authors claimed that their results were in accord with a reaction mechanism in which the dye molecule excited by the absorption of light was oxidised by the air, presumably with the initial formation of an azoxy group. If this is so, the nitrogen atoms in the azo group are acting as electron donors. This property will depend on the electrophilic nature of the substituent R, a positive σ value for R indicating a lower electron availability and hence a lower destruction efficiency k (i.e. a higher light fastness). However, the range of dyes which were used was deficient in members with substituents having positive σ values. It was therefore considered useful to extend the series of compounds examined to confirm the relationship between σ value and fading rate. Additional compounds of the type I have been prepared and examined by the technique reported by Atherton and Seltzer [1], and the measurements of the destruction efficiencies are reported here.

EXPERIMENTAL

The dyes were prepared as follows—the diazotised amine was added to a solution of α-naphthylamine in hydrochloric acid, the resultant mixture being slowly neutralised by the addition of sodium acetate. The dye was filtered off, and crystallised three or four times from a suitable

solvent. The purity of the dyes was such that they gave only one band when an alcoholic solution was run down a chromatographic column of activated alumina.

The casting and fading of the films were carried out in the manner described by Atherton and Seltzer[1], and the loss in concentration of the dye was plotted against the amount of light energy absorbed by the film, the experiments being carried out for a longer time than those in the previous paper. The general shape of the graphs so obtained was hyperbolic, although there were some exceptions, which gave a sigmoid curve showing an induction period. The initial rate of fading was determined by the gradient of the tangent at the origin for the normal hyperbolic curves or by the gradient at the point of inflexion for the sigmoid curves, i.e. the rate of fading after the induction period. From this datum the destruction constant was calculated. In Table I, the

TABLE I

Destruction Efficiencies of Substituted 4-Phenylazo-1-naphthylamines (I)

Substituent (R)	log (Relative Destruction Efficiency) (1)	(2)	Hammett's σ Value
p-O·CH$_3$	0·26 0·24	0·23	−0·268
p-CH$_3$	0·130	0·14	−0·170
m-CH$_3$	—	0·08	−0·069
m-O·CH$_3$	0·08 0·08	0·14	0·115
p-Cl	−0·36 −0·38	—	0·227
p-Br	−0·26 −0·40	—	0·232
m-Cl	−0·44 −0·36	—	0·373
m-NO$_2$	−0·25	0·09	0·710
p-CO·CH$_3$	−0·38	—	0·874
m-COOCH$_3$	−0·62 −0·46	—	0·355*
p-COOCH$_3$	−0·64 −0·67	—	0·728*
p-NO$_2$	—	0·46	1·27

* Hammett's σ values used are those quoted for the free acid.

results obtained in the present investigation are given in column (1) and those previously reported in column (2).

Each figure is the average of two experiments. It may be noted that the agreement between the present results and those of Atherton and Seltzer is good except for the compound containing a *m*-nitro group. The latter unfortunately shows irregular behaviour during fading.

DISCUSSION

The logarithm of the relative destruction efficiency is plotted in Fig. 1 against the σ value of the substituent. A straight line has been drawn through most of the points, and it shows that the relationship given by Atherton and Seltzer must be modified. The line is now steeper and passes through the origin. There are, however, three

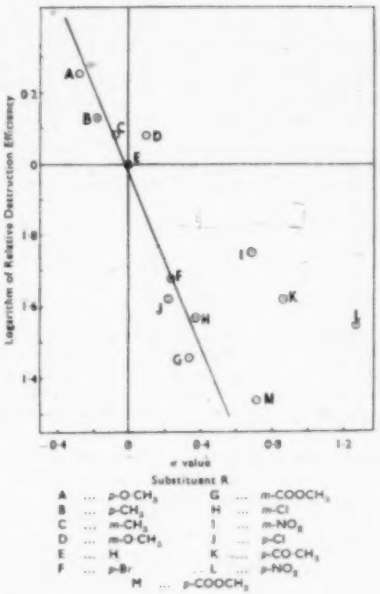


FIG. 1

compounds which do not fit on this line, although their fastness properties are in the order of their σ values, viz. R = *m*-NO$_2$, *p*-NO$_2$, and *p*-CO·CH$_3$. These compounds have a lower light fastness than that predicted by the straight line relation. These three groups have one property in common—that of easy reduction—in contradistinction to the groups contained in the other dyes. It is therefore possible that in these cases the first step in the fading process is an attack at the substituent group R to produce a compound more fugitive than the original.

Furthermore, if the fading reaction be dependent on the electron availability at the azo group, it follows that compounds with substituents in positions *ortho* to this group should have a higher light fastness, as the steric effect of the substituent would decrease the ease of attack on the azo group. The relative destruction efficiencies of some compounds with *ortho* substituents are given in Table II.

These results show some interesting points. The introduction of a small group such as methyl does not improve the fastness, whilst the larger methoxy does so. Thus, as may be expected, the steric effect is marked only for the larger substituents. If, on the other hand, the fastness of *p*-chloroaniline→α-naphthylamine coupled in the 2- and 4-positions be compared, that coupled in the 2-position has a considerably higher fastness than that coupled in the 4-position. Similar results are obtained for *p*-toluidine coupled to α and β-naphthylamine, the compound with the amino group *ortho* to the azo showing a greatly enhanced fastness. These results are in agreement with the

TABLE II

Compound	log (Relative Destruction Efficiency)
o-Toluidine→α-naphthylamine	+ 0·10
m-Toluidine→α-naphthylamine	+ 0·08
p-Toluidine→α-naphthylamine	+ 0·14
o-Anisidine→α-naphthylamine	+ 0·02
m-Anisidine→α-naphthylamine	+ 0·14
p-Anisidine→α-naphthylamine	+ 0·23
p-Chloroaniline→α-naphthylamine (coupled in 4-position)	− 0·21
p-Chloroaniline→α-naphthylamine (coupled in 2-position)	− 0·63
p-Toluidine→β-naphthylamine	− 0·37

hypothesis of an attack at the azo group, since it may be that, with the amino group in such a position, the azo group is protected possibly by hydrogen bonding between the hydrogen atoms of the amino group and the neighbouring nitrogen atom of the azo.

Summing up, then, the destruction of the dye seems to occur by attack at the azo group (although this may be complicated by a subsidiary reaction at a substituent group). This is shown by (*a*) the dependence of *k* on the σ value and (*b*) the steric effect of the *ortho* groups which hinder the fading reaction. Since, however, there is no conclusive evidence as to the exact nature of the reaction, it may be of value to summarise the modes of attack which could occur at the azo group. They are as follows—

(1) Direct addition of oxygen at the azo group to give peroxides or azoxy compounds—

$$-N=N- + O_2 \rightarrow -\overset{O}{\underset{|}{N}}=N- \text{ or } -\overset{O-O}{\underset{|}{N}}-N-$$

(2) Attack at the $=N\cdot C<$ linkage where the azo group is joined to the aromatic nuclei. This is possible, since the $=N\cdot C<$ linkage in *trans*-azobenzene has a considerable amount of double bond character, as shown by X-ray measurements [2].

(3) Formation of the phenylhydrazone form of the dye followed by attack by water and oxygen, as suggested by Desai and Giles [3].

(4) Reduction of the azo group by some electron transfer reaction with the substrate. A reduction mechanism has been suggested by Blaisdell [4]. Such a reaction would be markedly dependent on the substrate; for example, those substrates containing a large number of available hydrogen atoms or ions would show poorer light fastness. It would follow from this that dyes on oxycellulose would have worse light fastness than those on ordinary cellulose.

Unfortunately, there is insufficient evidence available to distinguish between these reactions.

CONCLUSIONS

The data presented in this communication augment those of Atherton and Seltzer[4] in establishing a relationship between σ value and light fastness, particularly for compounds whose substituents have positive σ values, since in the earlier work the compounds with positive σ values were nitro bodies. As was emphasised in the discussion at the 1949 symposium [1], the relationship between destruction efficiency and σ value is not exact. This may be largely accounted for by uncertainties in the related quantities, since both are obtained experimentally. One would not expect a strict relationship to hold, since σ value is a measure of the effect of some substituent group on the equilibrium point in one particular reaction (viz. dissociation of benzoic acids), and comparison with the reactivity of a molecule containing the substituent in some other system can be only approximate.

Of the dyes represented by positive σ values, three have lower light fastness than would be expected. This may be explained by the likelihood of a different type of photoreaction, which is specific to the chemical nature of the substituent and is not predictable in terms of the electronic effect at the azo link, since the three substituents in question are easily reducible.

* * *

The authors wish to thank D. Downey for assistance with the experimental work.

DYEHOUSE LABORATORIES
IMPERIAL CHEMICAL INDUSTRIES LTD.
HEXAGON HOUSE
MANCHESTER 9

(Received 17th August 1951)

References

[1] Atherton and Seltzer, J.S.D.C., **65**, 629 (1949).
[2] Robertson, *J.C.S.*, 232 (1939).
[3] Desai and Giles, J.S.D.C., **65**, 639 (1949).
[4] Blaisdell, *ibid.*, **65**, 618 (1949).

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

The Editor
SIR,

Action of Light on Vat-dyed Cellulose

The enhanced oxidation of cellulose, by exposure to light in the presence of atmospheric oxygen or other oxidising agents, brought about by certain vat dyes is by now well known. The exact course of the oxidation and the constitution of the resultant oxycelluloses are, in spite of a number of investigations which have been made, even now but imperfectly understood. When the dye is initially present as the leuco compound, and the oxidising agent is hypochlorite solution, the rate of oxidation of the cellulose is very rapid, and Nabar, Scholefield, and Turner [1] were able to show a constant ratio between the micro-Braidy copper number [2] and the Neale carboxyl value [3], independently of the total oxygen consumption and over the whole extended pH range. This pointed to a consistent oxidation mechanism, and

was not observed in the unaccelerated oxidation of undyed cellulose under similar conditions.

As a further investigation of the effects of prolonged exposure to light in the presence of oxygen, the following experiments have been made—Cambric made from Egyptian cotton was carefully scoured and bleached to obtain a thorough purification with minimum chemical modification. Dyeings were prepared using a variety of known tendering vat dyes in the usual manner, from a caustic hydrosulphite bath. Specimens were prepared by a corresponding treatment in a bath containing the same proportions of caustic soda and sodium hydrosulphite, but no vat dye was present. The two were separately soaped, washed well, and dried. All were then simultaneously exposed for long periods in the Atlas Fade-O-Meter (65% RH; 35°c.). After exposure, each dyeing was washed thoroughly in distilled water, and a portion treated with chlorous acid (0·1 M. sodium chlorite in 0·5 M. phosphoric acid) for 24 hr. at room temperature. Corresponding treated and untreated samples of each exposed pattern were then examined using the micro-Braidy method [2] for copper number determination, and by alkalimetry [3] and iodimetry [4] methods for the carboxyl value. The results of a few exposure trials are summarised in the accompanying table, in which the following values are given—(*a*) Free carboxyl groups (iodimetric method), (*b*) total copper number, (*c*) content of reducing groups (copper number) capable of oxidation to –COOH by chlorous acid, (*d*) carboxyl groups after treatment with chlorous acid, (*e*) content of alkali-sensitive reducing groups (copper number) not affected by chlorous acid, but capable of reducing Braidy solution to give copper number, (*f*) ratio of decrease in copper number to increase in carboxyl content after treatment with chlorous acid, and (*g*) ratio of decrease in copper number to residual copper number after treatment with chlorous acid.

It will be seen that the ratios (*f*) and (*g*) are all close to unity for exposed vat dyeings, but for exposed control "dyeings", in the absence of vat dyes, do not show the same relationship.

These results are very closely similar to those found by Nabar and Padmanabhan [5] for leuco dyeings of active vat dyes oxidised in the dark with dilute solutions of sodium hypochlorite under comparable conditions. The constant ratio of –CHO to –COOH found by Nabar, Scholefield, and Turner [1] for accelerated hypochlorite oxidation has been already mentioned.

Dyeing	Exposure (hr.)	Total –COOH formed (*a* m-equiv. per 100 g. cellulose)	Cu No. formed (*b*)	–COOH after Chlorite Treatment (*c* m-equiv. per 100 g. cellulose)	Cu No. after Chlorite Treatment (*d*)	Fall in Cu No. due to Chlorite Treatment ($e = b - d$)	$f = \frac{b-d}{c-a}$	$g = \frac{b-d}{d}$
Undyed control	144	0·96	0·96	1·69	0·52	0·44	0·60	0·85
	300	0·92	1·71	1·71	1·04	0·67	0·85	0·65
2% Cibanone Orange R	48	1·50	1·82	2·38	0·89	0·96	1·09	1·07
	96	2·40	3·13	3·98	1·52	1·61	1·02	1·06
	144	3·00	4·01	5·15	1·95	2·06	0·96	1·05
2% Cibanone Yellow R	144	3·91	4·80	6·30	2·46	2·34	0·98	0·97
2% Cibanone Yellow GC	144	1·83	2·63	3·12	1·30	1·33	1·03	1·02

It appears, therefore, that a similar product is obtained when cellulose is (*a*) oxidised very rapidly by sodium hypochlorite under the accelerating influence of the leuco form of an active vat dye in the dark or (*b*) oxidised by atmospheric oxygen more slowly by exposure to light in the presence of the same active vat dye. This appears to confirm the original suggestion of Scholefield and Turner [6] that the first effect of exposure to light of a dyeing of an active vat dye is to reduce the dye to its leuco compound, and that the subsequent course of the oxidation of cellulose (accelerated by the leuco compound), either by air or by hypochlorite, is the same.

These results will be discussed in greater detail later.

Yours faithfully

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G. M. Nabar

Department of Chemical Technology
University of Bombay
Bombay 19
India

5th December 1951

[1] Nabar, Scholefield, and Turner, J.S.D.C., **53**, 5 (1937).
[2] T. F. Heyes, *J.S.C.I.*, **47**, 90 T (1928).
[3] Neale and Stringfellow, *Trans. Faraday Soc.*, **33**, 881 (1937).
[4] Nabar and Padmanabhan, *Proc. Indian Acad. Sci.*, **31**, 371 (1950).
[5] Idem, *ibid.*, **32**, 232 (1950).
[6] Scholefield and Turner, *J. Textile Inst.*, **24**, P 130 (1933).

Notes

Proceedings of the Council

At a meeting of the Council held at the offices of the Society, 32-34 Piccadilly, Bradford, on 12th December 1951, the proceedings included the following items of interest—

SOCIETY'S MEDAL—A letter was read from Mr. W. Kilby, expressing appreciation and thanks for the award of the Gold Medal and stating that he accepted the award as a member of a team of investigators every one of whom had contributed to the successful development of the process.

NOMINATION OF OFFICERS—It was resolved unanimously that Mr. H. H. Bowen (President-elect) be nominated for election as President for 1952-53, and that Mr. H. Jennison and Mr. J. Barritt be nominated for election as Honorary Treasurer and Honorary Secretary respectively.

MEMBERSHIP—Nine applications for ordinary membership and three for junior membership were approved. Mr. B. R. Desai was re-admitted to membership of the Society.

Meetings of Council and Committees January

Council—9th
Finance—8th
Publications—15th
Colour Index Editorial Panel—7th
Reviews of Textile Progress—31st

Tentative Definitions

The Terms and Definitions Committee will welcome comments on the following tentative definitions—

3. HUE

The definition recommended by the Physical Society Colour Group (*Report on Colour Terminology*, No. 51, p. 9)—

That attribute of certain visual sensations by which we distinguish red, green, blue, yellow, purple, etc. from one another and by which the eye distinguishes different parts of the spectrum.

4. COLOUR VALUE

The ratio between the costs of the dyes yielding dyeings of equal visual strength.

5. TINCTORIAL VALUE

The intensity of colour obtained when a standard weight of dye is applied to a substrate under specified conditions.

6. EXHAUSTION

The ratio at any stated stage between the amount of dye or other substance taken up by the substrate and the amount originally available.

7. RATE OF DYEING

The rate at which a dye is absorbed by a substrate under specified conditions. It may be expressed quantitatively in several ways, such as the weight of dye absorbed in unit time, the percentage of dye absorbed in unit time, or the time taken for the substrate to absorb a given fraction of the amount of dye which it will absorb at equilibrium.

8. DISPERSE DYES

It is recommended that the term "dispersed dyes" be replaced by *disperse dyes*, as follows—

DISPERSE DYES are that class of water-insoluble dyes having substantivity for cellulose acetate and nylon, and usually applied from fine aqueous suspension.

Worshipful Company of Feltmakers

Sir George William Martin, K.B.E., LL.D., J.P., has been elected Master of the Company.

Change of Address of T.I.D.U.

The Technical Information and Documents Unit (D.S.I.R.) has been moved from Lacon House to Cunard Building, 15 Regent Street, London S.W.1 (*Telephone*—WHItehall 9788).

Soviet Conference on Molecular Structure

In the resolution[1] adopted by a conference on structural theory in organic chemistry held in June 1951 at Moscow, the theories of quantum-mechanical resonance and mesomerism are denounced as idealistic, mechanistic, sterile, and unsound. The Russian chemist Butlerov, who, in 1877, suggested the existence of what is now known as "tautomerism" to explain the behaviour of hydrocyanic and cyanic acids, is hailed as the founder of modern organic chemistry, and chemists are urged to take up "the further creative development of his theory of chemical structure on the basis of dialectical materialism". It is stated that Soviet chemists who have supported the theory of resonance have invoked it to explain all the facts and laws of chemistry, while trying to cover the unsoundness of the concept by reference to its alleged basis in quantum mechanics; they have thereby created a false feeling of well-being as regards structural theory and have held up true progress. At the conference supporters of the theory were called upon to recant. Amongst those who did so were Syrkin and Dyatkina, writers of a well known book on molecular structure that has been translated into English, and Kiprianov, well known for his work in dye chemistry. Their recantations were not, however, completely satisfactory, and it is recorded that in their addresses to the conference they failed to give a reasoned criticism of resonance theory and a detailed analysis of their serious methodological and ideological errors. It is urged that new textbooks and monographs that correctly portray the present state of chemical science should be published without delay.

A. E. STUBBS

[1] Abstracted from the resolution published in full in *J. Gen. Chem. U.S.S.R.*, **21**, 1729–1732 (Sept. 1951) and translated in *Nature*, **169**, 92–94 (19th Jan. 1952).

New Books and Publications

Die aromatischen Diazoverbindungen

By K. Holzach. Pp. 280. Stuttgart: F. Enke Verlag. 1947. Price, paper, DM 15.80.

Dr. Holzach was a student of E. Noelting, and from those days he has worked with diazo compounds and azo dyes. He spent his working life in the research laboratories of the Badische Anilin- & Soda-Fabrik at Ludwigshafen. His period of service fell in part during the time when with Caro as chief chemist the firm was developing its great range of azo dyes, and later his colleague Schraube, to whom this work is dedicated, gave further impetus to diazo chemistry by his discovery of the *iso*diazoates. This book, the first in German since that of Hantzsch and Reddelien in 1921, was written during the war after he had retired to Neckargemünd, and may therefore be held to crystallise the outlook of two generations of chemists of the B.A.S.F. on diazo compounds and the fundamental chemistry of azo dyes.

In the preface Holzach remarks that the history of the diazo compounds is divisible into three great periods. The first began with their discovery by Griess in 1858, and was followed by the great burst of development of the azo dyes and the replacement reactions blossoming from the work of Sandmeyer. Schraube's discovery in 1894 of the *iso*diazoates commenced the second, inducing the academic work in support of the controversies as to their structure. The third began with the work of Grieve and Hey and the school of Waters on the free-radical mechanism of reactions of the diazo compounds.

The book is divided into two parts— Part I, the diazonium salts, and Part II, the reactions of the diazonium compounds and diazohydroxides. Part I covers methods of diazotisation, the action of nitrous acid on diamines, polyamines, aminophenols and -naphthols, and diazotisable heterocyclic amines. This leads up to the properties of diazonium salts as such, e.g. colour, double salts, and stability as solids and in solution. The great controversy of the last half century concerning the constitution of the diazo compounds and the relationship of their various forms to one another is treated in seven pages toward the end of Part I and followed by paragraphs on nitrosoacylarylamides and quinonediazides. Part II commences with the arylhydrazines and arylnitramines, followed by the coupling reaction, which is subdivided into a section on compounds of the type of the diazosulphonates, diazocyanides, and diazoamino compounds and a section on the azo coupling reaction. This is the biggest single section in the book and contains much information on azo compounds, including reductive and oxidative scission. There follow the replacement reactions of the diazo compounds and a section on the action of light on diazonium salts and its application to diazotypes. As the author was cut off from British and American literature during the war, he added an appendix after this literature had become available to him. For the same reason there is no mention of Povay-Koshits and the Russian chemists. There are extensive author and subject indexes.

The literature of the diazo compounds is so vast and so closely woven into the literature of organic chemistry over almost the past century that no two authors are likely to agree on all the material to be included in a book such as this. The value of Holzach's book is that he has written chiefly about those aspects he knows from daily contact over a long life. K. H. SAUNDERS

Die neuzeitlichen Textilveredlungs-Verfahren der Kunstfasern

4. Lieferung

By F. Weber and A. Martina. Pp. 487–646. Vienna: Springer-Verlag. 1951. Price, 41s. 0d.

This, the fourth and penultimate instalment of this patent and literature review, covers the following subjects —water-repellent and waterproofing processes (75 pp.); finishing with solutions of cellulose and cellulose derivatives (5 pp.); laundryproof, Trubenised, and similar finishes (14 pp.); laminated fabrics including belting (8 pp.); flameproofing (12 pp.); weighting (2 pp.); wool-like finishes (4 pp.); pattern effects by mechanical and/or chemical finishes, e.g. moiré finish, use of alginate rayon as a scaffolding thread (6 pp.); various finishing agents (starches and their derivatives, synthetic polymers) and general finishing processes (8 pp.); coated fabrics including linoleum (oilskins and rubberproofing are dealt with under waterproofing) (18 pp.); pile fabrics including imitation furs (1 p.); hat finishing (2 pp.); desizing and degumming (3 pp.); and the commencement of the section on scouring. It is as a guide to the patent literature that this work is of greatest use, a particularly valuable feature being that it deals with the German patents and patent applications made during the war years, most of which have so far been available only to those able to spend the time and tedious labour necessary to search through the microfilms available (but with no index!) in the Patent Office Library. This alone makes the book well worth adding to the library of anyone interested in the subjects mentioned above. When completed the whole work will constitute a very valuable work of reference. C. O. CLARK

Spezial- und Hochveredlungsverfahren der Textilien aus Zellulose

By F. Weiss. Pp. vii + 211. Vienna: Springer-Verlag. 1951. Price, 38s. 6d.

This book is concerned essentially with the chemical finishing of cellulosic textiles; indeed, Dr. Weiss regards finishing as so much the chemist's domain that he entitles his last chapter "Mechanical Finishing as Substitute for Chemical Finishing". This chapter deals briefly with, among other things, the use of overfeed tenters and the Rigmel finish; to regard such processes as substitutes for chemical processes is, to say the least of it, rather peculiar.

As an introduction to the book there is an account by W. Reif of the chemical and physical properties of cellulose. Thereafter Dr. Weiss systematically deals with sizing and filling, softening, treatment with alkalis, treatment with acids and salts, finishing (including immunising and animalising) with organic compounds, use of scaffolding threads such as alginate rayon, crease-resistant finishes, diminishing the swelling properties of cellulose, under which heading dimensional stabilisation is dealt with, water-repellent finishes, delustring, flame- and rot-proofing. Each of these sections, with the exception of that on rotproofing, is adequately dealt with. The production of coated fabrics, oilskins, and combined fabrics is ignored. Dr. Weiss is concerned rather with principles than with details, which makes this book more suitable for use by teachers and students, to whom it can be recommended, than to the practical finisher, who however will find in it much that is of interest.

C. O. CLARK

Colour Cinematography

By A. Cornwell-Clyne. Third, revised and enlarged edition. 1951. Pp. xvi + 780 + 350 Fig. London: Chapman & Hall Ltd. Price, 84s. 0d.

The literature of colour photography and cinematography consists principally of a very great number of patents, and many papers dealing with limited sections of the subject, scattered over a wide range of often rather inaccessible journals. There are only a very few surveys of the whole subject, and the present volume is the only up-to-date one known to the reviewer. The second edition was published in 1939, and the advance of the subject since then has necessitated a considerable enlargment of the volume.

This will be a valuable reference work for all who are concerned with any branch of colour reproduction. It contains much detailed information upon e.g. the psychological and physiological phenomena of colour perception, the theoretical basis of colour reproduction, the mechanical construction of colour cameras, developing and printing machines, and projectors, chemical processes of colour image formation and colour development, the history of colour cinematography, etc. Some information is also given upon the use of dyes in printing colour films, which must now be a significant commercial outlet for specialised varieties of dye.

A most useful feature of this book is the large number of references to the original journal and patent literature.

C. H. GILES

Abstracts from British and Foreign Journals and Patents

(The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952); while other abbreviations and symbols, together with a list of the periodicals abstracted, will be found at the end of the annual index.)*

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Rapid Drying of Packages of Wound Yarn. H. Rieckenbach. *BP* 661,255

The packages are placed upon perforated tubes in an autoclave, and subjected alternately to the pressure of compressed air and sudden release of the pressure. This pneumatically wrings some of the water out of the packages, and after this water has been drained off drying of the packages is completed by blowing hot air through them.

C. O. C.

Molten-metal Dyeing Machine. Standfast Dyers & Printers. *BP* 661,086

Modification of *BP* 620,584 (*J.S.D.C.*, **65**, 412 (1949)), a treating liquor being made to float on the surface of the molten metal where the material leaves it. The presence of this liquor greatly reduces the tendency of the material to pick up scum or particles of the molten metal.

C. O. C.

Treating Two or More Tubular Fabrics alongside One Another. Samcor Holding Corpn. *BP* 661,167

Several rolls feed tubular fabrics to a washing or other processing machine. The rate of feed of each fabric is controlled by means of a spreader, the pressure on which actuates a device controlling the speed of the corresponding feed roll.

C. O. C.

Printing Machines. J. Dungler. *BP* 661,854

Easy, quick, and accurate adjustment of the contact width between the printing cylinder and the corresponding pressure or central pressure cylinder is obtained by having a conical bore at each end of the printing roller, each conical bore co-operating with a locking cone carried by a stub-shaft placed completely outside the roller and journalled in a bearing which can be displaced longitudinally.

BP 661,855

A chain stenter is arranged with a series of rotary printing machines so that the chains with gripping members are disposed above and below, respectively, the line of contact between the printing cylinders and the pressure cylinders. This permits high working speeds with ease of operation and adjustment. The printing obtained is constantly visible to the operative.

C. O. C.

Doctor Blade for Coating Apparatus. Champion Paper & Fibre Co. *BP* 662,099

A doctor blade of the type in which the wiping edge is a rotating rod is described.

C. O. C.

II—WATER AND EFFLUENTS

Nutritional Requirements during Aerobic Biological Stabilisation of Cotton Kiering Waste. E. N. Helmers and C. N. Sawyer. *Text. Research J.*, **21**, 671–680 (Sept. 1951).

The nitrogen and phosphorus requirements during the biological stabilisation of cotton kiering waste have been determined in order to provide a sound basis for the proportioning of flow to municipal plants or the addition of supplementary nutrients at industry-owned treatment plants.

A. B.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

***Bacillus prodigiosus* in Wool.** R. Steins. *Textil Praxis*, **6**, 703 (Oct. 1951).

A description is given of the results of an investigation on oiled wool exhibiting a pink coloration after a fortnight's storage. Microscopical examination and chemical tests traced the cause to the presence of bacilli in the vegetable mucilage constituent of the oil. A method for removal of bacterial contamination is included, and it is shown that the wool itself is not attacked. It is recommended that the oleine should be prepared with modern synthetic emulsifiers.

G. L.

Influence of Salt on Size and Shape of Protein–Detergent Complexes. J. A. Friend, B. S. Harrap, and J. H. Schulman. *Nature*, **168**, 910–911 (24 Nov. 1951).

Measurement of light-scattering is used to estimate the turbidity of protein–detergent solutions with and without NaCl, and the dissymmetry ratio of scattering gives information on the size and shape of the complexes. Diminution of turbidity with increasing detergent : protein or NaOH : protein ratio is supposed to be due to combination of protein (serum albumin) with detergent anions, resulting in a net negative charge on the protein. This charge also appears with alkali titration, and disappears in presence of salt. Dissymmetry ratios of 1·5–1·6 are observed with a molar detergent : protein ratio of 140, suggesting an unrolling of the protein molecule at these ratios; a more symmetrical configuration is adopted on adding salt. Dissymmetry effects vary according to the method of preparing the solutions. J. W. B.

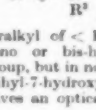
PATENTS

***N*-Acyl-*N*-alphyl Taurates having Surface-active Properties.** General Aniline. *BP* 661,701

Compounds of formula Alk·CO·NR·CH_2·CH_2·SO_3X (R = alkyl or *cyclo*alkyl; X = H, alkali metal, or NH_4; Alk + R must contain 15–18 C; Alk must contain 7–13 C; R must contain 5–8 C) have very high wetting power. C. O. C.

Detergents containing Fluorescent Agents. Procter & Gamble Co. *BP* 661,022

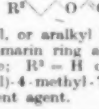
A mixture of (1) soap and/or an ionic and/or non-ionic synthetic detergent, (2) soap and/or an inorganic alkaline salt, and (3) a compound of formula—



(R^1 = H, Alk, or aralkyl *of* < 16 C; R^2 = OH, NH_2, NHAlk, $NAlk_2$, mono or bis-hydroxyalkylamino, or heterocyclic amino group, but in no case of > 6 C; R^3 = H or CH_3), e.g. 4-methyl-7-hydroxycarbostyril, is used as a detergent which gives an optical bleach.

BP 661,023

A compound of formula—



(R^1 = Alk, *cyclo*alkyl, or aralkyl having a sat. C atom adjacent to the coumarin ring and containing < 16 C; R^2 = same as above; R^3 = H or Alk of < 7 C), e.g. 3-benzyl(or *iso*propyl)-4-methyl-7-hydroxycoumarin, is used as the fluorescent agent. C. O. C.

Germicidal Detergent. F. C. Bersworth. *BP* 661,724

The germicidal activity of aqueous solutions of quaternary ammonium salts is increased by addition of alkali-metal salts of ethylenediaminetetra-acetic acid. When used in conjunction with inorganic detergents, e.g. phosphates, silicates, or carbonates, in presence of hard water no precipitate forms. C. O. C.

Fat-liquoring and Textile-softening Agents. Nopco Chemical Co. *USP* 2,555,684

Mixtures of an oleaginous softening material (20–240 parts by weight), water (not < 50), a sulphated aliphatic hydroxyalkylamide (20–80), and sulphated blown or unblown unsaturated fatty alcohol (80–20), the combined weight of the last two ingredients being 100 parts, are stable over a wide range of pH and can be used for fat-liquoring a wide range of leathers and furs; they are also excellent softening agents for textiles. C. O. C.

Whey as Agent for Treating Textiles and Leather. Plastica. *BP* 661,176

Whey containing milk-sugar, obtained as a by-product in the manufacture of cheese or milk-sugar, is a good auxiliary and finishing agent for leather and textiles, e.g. as protective colloid, or as sizing or tanning assistant. C. O. C.

Organosilicon Halides — Water-repellent Agents. British Thomson-Houston Co. *BP* 661,094

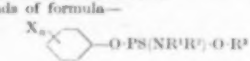
The products obtained by treating a compound of formula $Z_mSiR_nHal_{4-m-n}$ (Z = vinyl or allyl; R = a univalent hydrocarbon radical free from olefinic unsaturation; m = 1–4; n = 0–3) at 0–150°C. in presence of an organic peroxide with a silicon compound containing at least one H and at least one Hal attached directly to the Si atom, the remaining valencies of the Si atom being satisfied by H and/or Hal and/or univalent hydrocarbon radicals containing no olefinic unsaturation, are useful for producing a water-repellent finish by the process of *BP* 572,740 (*J.S.D.C.*, **62**, 159 (1946)). C. O. C.

Flame-retardant Compositions. DuP. *BP* 661,544

A mixture of polythene (50–62 parts by weight), antimony trioxide (20–35), and a solid chlorinated hydrocarbon containing 55–80% by weight of Cl (6–30) is an excellent flameproofing agent. C. O. C.

Insecticidal and Fungicidal Phenyl Amidothiophosphates. Dow Chemical Co. *BP* 662,024

Compounds of formula—



(X = Br or Cl; n = 1–5; R^1 = H or Alk; R^2 and R^3 = Alk or *cyclo*alkyl) are oils or crystalline solids, soluble in many organic solvents, insoluble in water, and having insecticidal and fungicidal properties. C. O. C.

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Simple Method of Preparation of *p*-Nitrobenzenesulphonyl Chloride. H. de Vries and T. A. Zuidhof. *Rec. Trav. chim.*, **70**, 696 (Sept.–Oct. 1951).

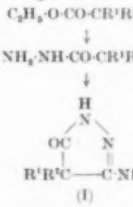
This is obtained in 80% yield by treating *p*-nitrothiophenol in acetic acid with chlorine saturated with water vapour. C. H. R.

Studies in the Elbs Persulphate Oxidation. II—Oxidation of α- and β-Naphthols and some Naphthol Derivatives. R. B. Desai and S. Sethna. *J. Indian Chem. Soc.*, **28**, 213–217 (April 1951).

Oxidation of α-naphthol, 2-acetyl-1-naphthol, and 1-hydroxy-2-naphthoic acid with potassium persulphate introduces a hydroxyl group into the 4-position. Under similar conditions β-naphthol and 2-hydroxy-3-naphthoic acid give 1:2-dihydroxy compounds. With 4′-methyl-1:2-naphtho-α-pyrone and 4′-methyl-2:1-naphtho-α-pyrone the hydroxyl group appears to go into the 6-position. The yields, except in the cases of α-naphthol and its derivatives, are very poor. C. H. R.

Synthesis and Ultraviolet Absorption of 3-Amino-5-pyrazolones. F. E. Gagnon, B. Molin, and R. N. Jones. *Canadian J. Chem.*, **29**, 843–847 (Oct. 1951).

3-Amino-5-pyrazolones substituted in the 4-position are synthesised from substituted cyanoacetic esters, by formation of the corresponding acetohydrazides followed by ring closure—



(I)

Monosubstituted compounds (R^1 = H; R^2 = *n*-hexyl, *n*-heptyl, *n*-decyl, 2-ethyl-*n*-butyl, 2-ethyl-*n*-hexyl, *cyclo*hexyl, or α-naphthylmethyl) are prepared from the corresponding hydrazides with strong caustic soda. 4-Acetohydrazido-3-amino-5-pyrazolone and 4:4-disubstituted compounds (R^1 = R^2 = methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-amyl) are prepared from disubstituted cyanoacetic esters and hydrazine hydrate. All are sol. in water, acids, and alkalis, and insol. in ether and $NaHCO_3$ soln. All give

a positive colour test for the presence of a potential hydroxyl group with ferric chloride, and the amino group reacts with nitrous acid. The ultraviolet absorption spectra are measured in neutral and acidic ethanol. The monoalkyl, dialkyl, *cyclo*hexyl, and α-naphthylmethyl derivatives give similar spectra, with an absorption max. at ca. 2800 A., supporting formula I with the cyclic double bond in the 2:3-position. The spectrum of 4-aceto-hydrazido-3-amino-5-pyrazolone has an absorption max. of higher intensity at a shorter wavelength (ca. 2400 A.); the cyclic double bond may be in the 3:4-position. A. J.

Reaction of Diazo Compounds with Bisalkyl-sulphonylmethanes. H. J. Backer. *Rec. Trav. chim.*, **70**, 733–737 (Sept.–Oct. 1951).

1:1 Methylene disulphones give with an excess of a diazo compound a yellow azo product (I), together with a small amount of a substance, the structure of which is given as II. A mechanism for the formation of II from I is postulated. With a large excess of diazo compound a substance given the structure III is also obtained.

$$R^1\cdot N{:}N\cdot CH(SO_2\cdot R^1)_2$$
(I)

$$R^1\cdot SO_2\cdot CH(N{:}N\cdot R^1)\cdot O\cdot C(N{:}N\cdot R^1)_2\cdot SO_2\cdot R^1$$
(II)

$$R^1\cdot N{:}N\cdot CO\cdot N{:}N\cdot R^1$$
(III)

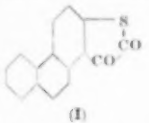
C. H. R.

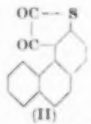
Studies on Coal-tar Colours. IX—Preparation, Purification, and Determination of D&C Yellow No. 7, D&C Orange No. 5, D&C Red No. 21, Tetrachlorofluorescein, D&C Red No. 27, and FD&C Red No. 3. M. Dolinsky and J. H. Jones. *J. Assocn. Off. Agric. Chem.*, **34**, 114–126 (1951): *Chem. Abs.*, **45**, 9271 (25 Oct. 1951).

The preparation and purification of these dyes are described. Analytical data obtained on the purified dyes are given. Spectrophotometric data obtained on dilute aqueous soln. of the dyes are provided as an aid in their identification and analysis. C. O. C.

Azine Dyes derived from 1:2- and 3:4-Phenanthrathiophen-2':3'-diones. D. N. Chaudhury and P. C. Dutta. *J. Indian Chem. Soc.*, **28**, 175–178 (April 1951).

1:2- (I) and 3:4-Phenanthrathiophen-2':3'-diones (II), obtained from the corresponding thiols, have been condensed with o-phenylenediamine, 2:3-diaminoquinoxolin, and 2:3-diaminophenazine. The azine compounds obtained gave yellows to browns on wool.

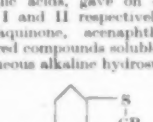

(I)

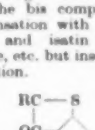

(II)

C. H. R.

Indigoid Dyes. XII—Phenanthrathiophen-indigos. P. C. Dutta and D. N. Chaudhury. *J. Indian Chem. Soc.*, **28**, 169–174 (April 1951).

1:2-Phenanthra-2'-ketodihydrothiophens (I: R = H_2) and the 3:4-compound (II: R = H_2), obtained from the corresponding phenanthrenethiols through their thioglycollic acids, gave on oxidation the bis compounds (R = I and II respectively). Condensation with phenanthraquinone, acenaphthaquinone, and isatin gave coloured compounds soluble in pyridine, etc. but insoluble in aqueous alkaline hydrosulphite solution.


(I)


(II)

C. H. R.

Absorption Spectra of Thioindigo Dyes in Benzene and Chloroform. W. R. Brode and G. M. Wyman. *Bur. Stand. J. Res.*, **47**, 170–178 (Sept. 1951)—*Research Paper* 2241.

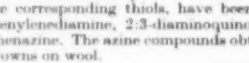
The ultraviolet and visible absorption spectra of eight purified thioindigo dyes are measured in benzene and chloroform soln. after prior exposure to light of varying wavelengths. The experimental absorption spectra are compared with the most probable calculated curves for each pair of *cis* and *trans* isomers, and an equilibrium is indicated which is affected by illumination. In general the first (long-wave) absorption band of the *cis* form occurs at a shorter wavelength (ca. 60 mμ) than that of the *trans* form. The spectra in chloroform are displaced to slightly longer wavelengths compared with benzene. Substituents in the 5- and 7-positions cause a bathochromic shift in all cases. Substituents in the 4- and 6-positions give a change in the shape of the absorption curves and a hypsochromic shift, possibly owing to stronger conjugation with the negatively polarised oxygen atoms in the second excited state. The present paper is an extension of previous work (Wyman and Brode, *J. Amer. Chem. Soc.*, **73**, 1487 (1951)). A. J.

Studies in the Cyanine Dye Series. XI—The *mero*-Cyanines. L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. Van Dyke, E. Van Lare, G. Van Zandt, and F. L. White. *J. Amer. Chem. Soc.*, **73**, 5327–5332 (Nov. 1951).

Various methods are described for preparing *mero*-cyanine dyes, i.e. dyes characterised by the amide resonance system—

$$>N\cdot[C{:}C]_n\cdot C{:}O \longleftrightarrow >\overset{+}{N}{:}[C{:}C]_n\cdot C\cdot O^-$$

In these dyes the N and CO "ends" of the amide system are generally included in rings—



although compounds having the CO end in an open-chain system need not be excluded from the class. The dyes vary from almost colourless to greenish blue; many of them are strong photographic sensitisers. Details are given of 32 syntheses. C. O. C.

Mathematical Treatment of the Colour of the *mero*-Cyanine Dyes. W. T. Simpson. *J. Amer. Chem. Soc.*, **73**, 5359–5363 (Nov. 1951).

Long-wavelength singlet–singlet electronic transition energies and intensities are calculated for the *mero*-cyanines by use of a valence-bond type method and an equivalent single-particle model. The characteristic shift to short wavelengths of absorption, with diminution of intensity, for non-polar *mero*cyanines in solvents of decreasing dielectric constant is obtained. An initial shift of absorption to long wavelengths is predicted to occur with the first decrease of dielectric constant, or what is equivalent, a negative Brooker deviation is predicted to occur for unsymmetrical cyanines in which there is only a slight defect in the symmetry of the extreme resonance structures. A qualitative understanding of these results is facilitated by use of perturbation theory in conjunction with the single-particle model. C. O. C.

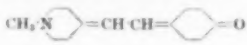
Colour and Constitution. X—Absorption of the *mero*Cyanines. L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. Van Dyke, E. Van Lare, G. Van Zandt, F. L. White, H. W. J. Cressman, and S. G. Dent. *J. Amer. Chem. Soc.*, **73**, 5332–5350 (Nov. 1951).

In a *mero*cyanine an additional double bond enters each of the two rings of the dye in the dipolar resonance with $>\overset{+}{N}\cdot C\cdot[C{:}C]_n\cdot O^-$. Depending on the rings paired in the dye, stabilisation thus acquired may be low, high, or of any intermediate value. If such stabilisation is low, the dye has low intrinsic polarity: it will show large λ_{max} deviations in all solvents, and λ_{max} will tend to shift to longer wavelengths with increasing polarity of the solvent, especially for the higher vinylogues of a series. If stabilisation is moderate, the dye may show negligible deviation in a solvent of moderate polarity, e.g. methanol, and λ_{max} will be relatively insensitive to change of solvent. If stabilisation is great, the dye has high intrinsic polarity, shows small deviations only in solvents

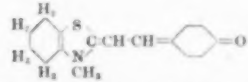
of low polarity, and exhibits extraordinary shifts of λ_{max} to shorter wavelengths with increasing polarity of the solvent, these shifts increasing with chain length. C. O. C.

Colour and Constitution. XI— Anhydronium Bases of *p*-Hydroxystyryl Dyes as Solvent Polarity Indicators. L. G. S. Brooker, G. H. Keyes, and D. W. Heseltine. *J. Amer. Chem. Soc.*, **73**, 5350–5356 (Nov. 1951).

Two exceedingly polar *merocyanines*—



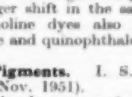
and



for which the dipolar structures dominate even in pure pyridine solution, show such large shifts of λ_{max} to shorter wavelengths on increasing the polarity of the solvent (by adding water) that they can be used for the colorimetric determination of water in pyridine or *vice versa*. For each of a number of somewhat less polar *merocyanines*, a characteristic change of direction in the absorption maximum–solvent composition curve (of pyridine–water mixtures) occurs at a point where the extreme resonance structures are thought to be energetically equivalent. On one side of this point the uncharged structure dominates, whereas the dipolar structure dominates on the other. C. O. C.

Colour and Constitution. XII— Absorption of the Phthalones. L. G. S. Brooker and G. H. Keyes. *J. Amer. Chem. Soc.*, **73**, 5356–5358 (Nov. 1951).

The shift of λ_{max} to shorter wavelengths shown by *N*-methylpyrophthalone—



in passing from chloroform as solvent to water (Kuhn and Bär, *Annalen*, **516**, 155 (1935)) is characteristic of strongly polar *merocyanines*. The higher vinylogue of this compound shows a larger shift in the same direction. The corresponding quinoline dyes also show these shifts, as do pyrophthalone and quinophthalone themselves. C. O. C.

Phthalocyanine Pigments. I. S. Moll. *Paint*, **21**, 402–406, 418 (Nov. 1951).

A review of the development and uses of the phthalocyanine pigments. 17 references. C. O. C.

Chemical Composition of the Red Eye Pigment of *Drosophila melanogaster*. F. L. Chan, H. Heymann, and C. W. Clancy. *J. Amer. Chem. Soc.*, **73**, 5448–5449 (Nov. 1951).

Lederer's suggestion (*Biol. Rev. Cambridge Phil. Soc.*, **15**, 273 (1940)) that these pigments are pterine derivatives receives confirmation. C. O. C.

Action of Light on Colouring Matters and their Oxidation. N. R. Dhar. *Proc. Natl. Acad. Sci. India*, **18A**, 65–87 (1949): *Chem. Abs.*, **45**, 8897 (25 Oct. 1951).

Basic dyes usually contain many C and H atoms, behave as weak reducing agents, and are oxidised by atmospheric O_2 especially in presence of light and so become faded. Generally they have smaller mol. wt. than acid dyes; the greater the mol. wt. of a dye, the greater its stability to photo-oxidation. Acid dyes contain more O than basic dyes and are not oxidised by O, as much as are basic dyes. Acid dyes in water exist as either finely divided insoluble particles or as colloidal aggregates, while basic dyes in aqueous solution are usually in molecular condition. Natural dyes contain more O than synthetic basic dyes, and resist photo-oxidation, especially when in the colloidal state or protected by other colloids. When fluorescent and non-fluorescent dyes in alcoholic and aqueous solutions are oxidised by O_2 or H_2O_2 and $FeSO_4$ the glow observed is much more pronounced with the fluorescent dyes. Fading of fluorescent dyes is not caused by their fluorescence but by photo-oxidation or photodecomposition. A dye can fade because of photodecomposition, photo-oxidation by the air, or photoreduction by the fibre or mordant. Photosensitising dyes act as marked absorbers of visible light and have a reducing action on silver halides; they are usually basic dyes. Photographic desensitisers are also good absorbents of light, but do not reduce silver halides. The desensitising effect is chiefly due to complete absorption of light by the desensitising dye, thus preventing the light from reaching the silver halide. In the case of some desensitisers the absorbed light breaks up the desensitising molecules and is completely dissipated before it can reach the silver halide particles. C. O. C.

Review of Pigment Progress 1950–51. W. M. Morgans. *Paint*, **21**, 397–401, 423 (Nov. 1951).

A review concerned mainly with inorganic pigments. 96 references. C. O. C.

Ferruginous Earths, Ochry Clays, Boles, and Ochres. H. Rabaté. *Trav. Peint.*, **4**, (8), 62–63 (1948): *Chem. Abs.*, **45**, 9277 (25 Oct. 1951).

L'Association française de Normalisation has adopted the following definitions— *Earths*— Natural mineral pigments obtained by simple physical treatment of rocks, generally less bright than artificial pigments, composed for the greater part of iron oxide fixed on clayey matter. *Ochres*— Natural mineral pigments, yellow or red, raw or calcined, composed of Fe_2O_3 more or less hydrated, fixed on a complex (badly defined) of SiO_2 and hydrated Al_2O_3. C. O. C.

Composition of Complex Ferric Ferrocyanide (Prussian Blue) by Potentiometric Method. A. K. Bhattacharya and R. S. Saxena. *J. Indian Chem. Soc.*, **28**, 221–224 (April 1951).

The composition of Prussian Blue determined by a potentiometric method using a ferricyanide–ferrocyanide electrode approximates to $KFe[Fe(CN)_6]$, but is influenced by hydrolysis and adsorption. C. H. R.

PATENTS

***cyclo*Hexylylammonium Salts of Dye Acids.** Allied Chemical & Dye Corpn. *USP* 2,555,603

The *cyclo*hexyl*cyclo*hexylammonium salts of dyes containing one or more sulpho or carboxyl groups have better solubility in alcohol than the free dye acids; e.g. the 2-amino*cyclo*hexyl*cyclo*hexane salt of Naphthol Green B (*C.I.* 5) is insoluble in water and hydrocarbons but soluble in alcohols. C. O. C.

Pearl-effect Materials. BrC. *BP* 662,018

Material suitable for imparting pearl effects to plastics is produced by stirring aqueous mercuric chloride into an aqueous alkali-metal phosphite at pH 5–9, filtering the precipitated minute crystals, and washing with water containing a substance which prevents agglomeration of the crystals, e.g. a protective colloid, a Ca salt of hydrolysed fish-scale protein, or an anionic wetting agent. Pearl essence is produced by giving the crystals a final rinse in a water-soluble organic liquid and suspending them before they are completely dry in a dilute solution of a thermoplastic derivative of cellulose. C. O. C.

V— PAINTS; ENAMELS; INKS

Wet-ground Mica. Anon. *Paint*, **21**, 407–411 (Nov. 1951).

An account of work recently done by a team of workers led by M. Kronstein at New York University. It deals *inter alia* with the use of wet-ground mica as an extender in paints and resin-based coatings. C. O. C.

PATENTS

Safety Ink. J. de Vries. *USP* 2,555,474

An ink which gives a well defined colour if attempts are made to bleach it with oxidising or reducing agents consists of a mixture of 1 oz. aniline dye, e.g. Methylene Blue, Methyl Violet, or Malachite Green, in 1 gal. water, 1 oz. cobaltous chloride in 1 pint water, and 1 gal. of a sat. aq. soln. of benzidine dihydrochloride. C. O. C.

Polyvinyl Acetate Emulsion Paints. Shawinigan Products Corpn. *BP* 657,545

Polyvinyl acetate emulsion paints, as prepared e.g. according to *BP* 615,723, show improved adhesion and

washability on addition of 10–20% on the polymer of an oil modified alkyd resin, a polyterpene, a coumarone–indene resin, or a rosin ester to emulsions in which the particle size x is $< 5\ \mu$, the percentage of emulsifier y is < 10, and the values are those which satisfy the equation $x(y - 0{\cdot}5) = 9$. E. C.

Polyvinyl Resin Coatings for Metals. Bakelite Corpn. *BP* 657,867

Water-insoluble partial esters, ethers, or acetals of polyvinyl alcohol, e.g. polyvinyl acetate–alcohol, show improved adhesion to metals when treated in solution, e.g. in ethanol or acetone, with an aqueous mixture of 4–12% phosphoric acid and less (2–6%) chromium trioxide. E. C.

Baking Metal Powder Silicate Coatings. Industrial Metal Protectives. *USP* 2,555,587

The coating is first dried and then set by moving a brush flame at 6300° F. across the coating at the rate of 10 ft./min. C. O. C.

Sheep-branding Fluids removable by Scouring (VII p. 75).

VI—FIBRES; YARNS; FABRICS

Microscopical Investigation of the Swelling of Native, Bleached, or Nitrated Cellulosic Fibrils or Fibres. G. Mangenot and M. Raison. *Rev. Cytol. Cytophysiol. vegetales*, **6**, 1–83 (1942–3): *Chem. Abs.*, **45**, 9272 (25 Oct. 1951).

Following a review of the literature (78 references) a method of determining structure and swelling is described, in which the fibre surface is nitrated and then gelatinised with a neutral solvent. The appearance (under low-power magnification) of natural, bleached, or nitrated cotton fibres under different physical and chemical conditions (especially treatment with Schweitzer's reagent or stains) is given. Schweitzer's reagent was also used in examining fibres of sorghum (*Sorgum vulgare*), arundo (*Arundo donax*), and ramie (*Bahmeria nivea*), both native and nitrated. The solvent and gelatinising action of cyclopentanone, hexane, castor oil, acetone, methyl alcohol, methyl nitrate, methyl acetate, diethylene glycol nitrate, and nitroglycerin on native, and on mono-, di-, and tri-nitrated cotton is considered in detail. C. O. C.

Degradation of Cellulosic Fibres. K. Schwertassek. *Melliand Textilber.*, **32**, 774–778 (Oct. 1951).

The degradation of cellulosic fibres under varying conditions is studied, including—damage by chlorination and sulphuric acid to viscose rayon staple, mercerisation of various cellulosic rayons, drying of rayons under varying conditions, effect on iodine values of anti-swelling treatments such as the resin-formaldehyde treatment, comparative iodine values of nitrate, acetate, and viscose rayons. B. K.

Paper Chromatography of Flax Fibre Polyuronide Hemicellulose. G. C. Whiting. *Nature*, **168**, 833–834 (10 Nov. 1951).

Paper chromatography of flax fibre hemicellulose hydrolysate shows the presence of arabinose, xylose, galactose, glucose, mannose, rhamnose, and traces of two other substances. J. W. B.

Progressive Delignification of Jute Fibre with Chlorine Dioxide. A. B. Sen Gupta and H. J. Callow. *J. Textile Inst.*, **42**, T 375–T 384 (Sept. 1951).

An attempt has been made to remove lignin progressively from jute fibre with chlorine dioxide solution without disturbing, as far as possible, the carbohydrate portion and without destroying the fibre structure. The original lignin content is determined (idem, *ibid.*, **40**, T 650 (1949)); then the sample is treated in a stoppered flask with chlorine dioxide at room temperature for 24 hr., and washed with hot water to remove ClO_2 and degradation products. The sample is partly dried and reconditioned, the moisture content determined by drying to 105°C., and the residual lignin estimated as before. pH of ClO_2 has little effect on quantity of lignin removed. The loss in weight is smaller than the loss of lignin, owing to incomplete removal of decomposition products. By using sodium bisulphite, neutral sodium sulphite, and alkaline sodium sulphite respectively in the hot-water wash, there is a progressive increase in lignin removal up to a concn. of 0·50% ClO_2. At 0·98% ClO_2 variation of washing does not alter lignin removal. Increasing ClO_2 concn. from 0·25 to 0·98% increases amount of lignin removed. Alkaline and neutral sulphite wash liquors, although removing more lignin than bisulphite, also remove more hemicellulose, and their use is not recommended. Temperature of ClO_2 soln. has a marked effect on lignin removal, and treatment at a controlled temperature is necessary to obtain reproducible results.

The modification of carbohydrate by drying to 105°C. and by treatment with ClO_2 has been studied, and it has been found that both treatments have a small effect. Also the possibility of residual lignin being modified or of degradation products being retained has been examined, and it is shown that partly delignified jute retains tenaciously some of the bisulphite used for removing the degradation products. Fairly satisfactory partial delignifications of jute can be made with dilute solutions of ClO_2, though the loss in weight tends to be lower than the loss of lignin, and possible reactions of ClO_2 with the components of jute have been studied in order to throw some light on this difference. A. H.

Resistant Peripheral Membranes of Keratin Fibres. E. H. Mercer, C. H. Bamford, A. Elliott, and W. E. Hanby. *Nature*, **168**, 824–825 (10 Nov. 1951).

Claims by Alexander and Earland, and Happey, regarding the isolation and constitution of a resistant wool surface membrane are criticised and discussed by Mercer, Bamford *et alia* contest Mercer's views. J. W. B.

Structural Orientation in Cellulose Acetate Filaments and the Dichroism of Adsorbed Dyes. D. R. Morey and E. V. Martin. *Text. Research J.*, **21**, 607–620 (Sept. 1951).

The relation of the structural orientation of cellulose acetate filaments to the dichroism of adsorbed dyes has been studied. X-Ray reflection data are used as standard, and the derivation of a method of computing the percentage orientation from the density of the 002 ring is given. The method of determination of orientation by means of dichroic dyes is detailed, and a list of experimental and commercial dyes is given, classified according to the degree of dichroism shown. The conditions of dyeing are shown to affect the observed dichroism. The percentage orientation as measured by dichroism is found to be less than that obtained from X-rays, indicating that the former takes amorphous material into account. A. B.

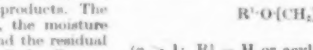
Static Electrification of Nylon — Reduction by Inhibitors. G. W. Graham. *Nature*, **168**, 871–872 (17 Nov. 1951).

Quantitative measurement of static on nylon is effected by rubbing a hank over three metal rods, the outer steel ones being earthed and the central one being of brass and connected to one terminal of a voltage-measuring device. Results are illustrated showing the effect of five different lubricants, two types of curve being obtained. The smooth type shows variation of charge with dielectric constant of liquid, water (high dielectric constant) being very effective in reducing static. Surface-active agents give a periodic type of curve, though with the same overall trend as the smooth type. This is considered as due to the formation of molecular layers, with alternating orientation of dipoles giving corresponding reversal in sign of electrical charge. The most effective agents are those which combine (*a*) a dipole strong enough to limit the field due to nylon within several layers of the surface and (*b*) a degree of surface activity which allows random orientation at small amounts. A mechanism is suggested. J. W. B.

PATENTS

Copolymeric Linear Esters. Courtaulds. *BP* 660,883

Fibre-forming esters are obtained by heating (*a*) a compound of formula—



($n > 1$; R^1 = H or acyl; R^2 = H or Alk of < 7 C), e.g. *p*-β-hydroxyethoxybenzoic acid), and (*b*) a compound of formula—

(R^3 = H or acyl; R^4 = H or Alk of > 7 C), e.g. *p*-acetoxy-

benzoic acid. The polyesters may be formed by intermolecular condensation of (*a*) and (*b*) or by heating this copolymeric ester with (*a*) or a polymer obtained by autocondensation of (*a*). W. G. C.

Polythioureas. Courtaulds. *BP* 660,905

The fibre-forming polythioureas obtained by treating CS_2 with a diamine $H_2N{\cdot}(CH_2)_n{\cdot}NH_2$ ($n > 2$) in aqueous emulsion have higher intrinsic viscosity and are less discoloured than the products of reaction in solution. W. G. C.

***NN*-Dimethylpropionamide — Solvent for Acrylonitrile Copolymers.** Monsanto. *BP* 660,702

NN-Dimethylpropionamide is a good solvent for the copolymers of acrylonitrile (75–97%), methacrylonitrile (18–2%), and vinyl acetate (18–2%), and is useful in the wet spinning of synthetic fibres from these copolymers. W. G. C.

Wet-spinning Acrylonitrile Polymers and Copolymers. DuP. *USP* 2,555,300

Polyacrylonitrile or a copolymer containing not < 80% acrylonitrile is dissolved in a high-boiling water-soluble solvent, and the solution extruded into hot glycerol; the resulting filaments are passed through a water dip and then wound. If desired a second passage through hot glycerol may be interposed between the water dip and winding. The yarn is then washed, dried, stretched, and heated in air. Because of quicker congulation higher spinning tensions can be used, and so yarn of higher tenacity is formed. C. O. C.

Spinning Rubber Thread. Redding Manufacturing Co. *BP* 660,983

Rubber thread can be formed by discharging under pressure a continuous stream of latex into the centre of a viscously flowing supporting and confining liquid stream whose central portion moves in the same direction and at substantially the same speed as the latex. The viscous liquid may be hot glycerol, which hardens the latex by the combined action of heat and dehydration to form a continuous latex thread. W. G. C.

Bacillus prodigiosus in Wool (III p. 70).

Production and Dyeing of Coconut Yarn (VIII this page).

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Synthetics in Cotton Detergency. H. L. Sanders and J. M. Lambert. *Text. Research J.*, **21**, 680–684 (Sept. 1951).

A mixture of phosphates, carboxymethyl cellulose, and synthetic detergents is shown to wash cottons about as well as soap does. The mechanism of the action of these additives is discussed, and it is concluded that it is probably due at least in part to adsorption of the phosphate ion, which modifies the charges on soil and fabric, and also to a mechanical blocking action of carboxymethyl cellulose at the fibre interstices. A. B.

Sheep-branding Fluids removable by Scouring. M. Lipson. *Australian J. Applied Sci.*, **2**, 200–204 (1951): *Chem. Abs.*, **45**, 9199 (25 Oct. 1951).

A satisfactory fluid consists of lanolin (4 parts), rosin (2), and stearic acid (1) emulsified in water with NH_4 stearate and Monolite Scarlet, Monastral Blue, or a lacquer black. C. O. C.

Dry Cleaning Processes. G. P. Fulton. *Amer. Dyestuff Rep.*, **40**, P 739–P 742, P 744 (12 Nov. 1951).

An account of dry cleaning processes, including problems involved, e.g. new materials, wet cleaning, mothproofing, and water repellency. J. W. B.

Progressive Delignification of Jute Fibre with Chlorine Dioxide (VI p. 74).

VIII— DYEING

Fault in Direct-dyed Cotton Fabric. Anon. *Teintex*, **16**, 493–495 (Sept. 1951).

An unusual fault consisted of a number of small dark patches on the dyed pieces. After careful examination the grey pieces were found to contain small particles of leather which had been trapped between the warp and weft during weaving. When the cloth was wet-processed the leather disintegrated and released chromium salts, which modify the colour of many direct dyes. F. A.

Photochemical Dyeing by the Vat Craft Method. L. E. Ravich. *Textil Praxis*, **6**, 669–672 (Sept. 1951).

Fundamental principles are described and the historical development is traced. Indigosols are hydrolysed to their leuco forms by irradiation, and then oxidised to insoluble pigment-dyes. Presence of traces of sensitisers is essential. Details of plant used are given. It is claimed that uniform dyeing is obtained with many types of fibre mixtures, since the method is independent of the chemical nature of the substrate. G. L.

Dyeing of Carpet Yarns. G. Kittan. *Textil Praxis*, **6**, 676–679 (Sept. 1951).

The paper claims to survey recent developments in this field. Machinery considered suitable in individual cases is described, and a critical discussion of dyeing methods follows with special reference to union materials. G. L.

Production and Dyeing of Coconut Yarn. H. Faldik. *Textil Praxis*, **6**, 683–684 (Sept. 1951).

Origin, production methods, and properties of coconut yarn are briefly described. Dyeing is carried out in the unbleached state using basic, acid, direct, or bisulphite-solubilised dyes. The material is stated to be suitable for carpets and furnishings, showing good moisture resistance and ease of soil removal. G. L.

Dyeing of Perlon. W. Ender. *Melliand Textilber.*, **32**, 780–784 (Oct. 1951).

The most important classes of dyes for various textile fibres and the main chemical and physical properties of these fibres which are of significance in dyeing are given in tabular form. The dyeing of nylon and Perlon is discussed, and the effect of acid treatment under varying conditions on the tensile strength and elasticity of Perlon is given. B. K.

Dynel Fabrics — Dyeing and Wet Finishing. T. A. Feild. *Amer. Dyestuff Rep.*, **40**, P 737–P 738, P 744 (12 Nov. 1951).

The heat sensitivity of dynel (vinyl chloride–acrylonitrile copolymer) necessitates careful cooling of hot dyebaths to avoid wrinkling or creasing, though high shrinkage in dyeing can be used to simulate wool felting. Above 205°F. the fibre becomes delustred but may be relustred by raising to 240°F. for a short time or by boiling in 6% sodium sulphate. Dyeing is best done at 205°F. or above. Acetate rayon dyes are dispersed with 1% agent, and are usefully maintained thus by a high pH; a 1-hr. boil is followed by scouring at lower temp. An intermediate sodium sulphate treatment assists exhaustion and maintains lustre. Basic dyes are applied using acetic acid as assistant. Acid dyes are assisted either by *p*-phenylphenol at pH 6 or by using a cuprous salt, e.g. *in situ* from $CuSO_4$ and zinc formaldehyde-sulphoxylate. Both may be used together for very heavy dyeings. Direct cotton dyes are applied by acid dyeing procedures, and work has also been done on applying soluble vat, vat, and pigment dyes. J. W. B.

Dyeing of Rhovyl. M. Rampin. *Teintex*, **16**, 519–521 (Oct. 1951).

A large number of acetate rayon dyes of Continental manufacture have been examined for their suitability for dyeing Rhovyl. A list is given of 47 dyes which give good colour value on Rhovyl and have a fastness to light of at least 3–4. They are dyed in presence of Product AC8 by the method described in *Teintex*, **15**, 521 (1950). F. A.

PATENTS

Dyeing and Printing Cellulose Esters and Ethers. S. *BP* 661,800

Fast-to-washing dyeings or prints are obtained with acid dyes on cellulose esters or ethers if to the dye liquor or printing paste there is added a volatile aliphatic carboxylic acid, an aliphatic hydroxylated compound, and 3% by weight of the liquor or paste of a thiocyanate, urea, thiourea, or guanidine. The dyed or printed material is dried at 40–50°C., washed with cold water, and finally soaped at 60°C. C. O. C.

Colouring Cloth with Aqueous Pigment-Lacquer Emulsions. IC. *BP* 661,085

The cloth is treated with an aqueous emulsion of a pigmented lacquer (the binder being not > 2·5% of the

emulsion, not < twice the volume of the pigment, and consisting of a thermohardening synthetic resin, and the lacquer solvent having vapour pressure not > 28 mm. at 25°c.), dried, and finally baked. C. O. C.

Structural Orientation in Cellulose Acetate Filaments and the Dichroism of Adsorbed Dyes (VI p. 74).

IX—PRINTING

Influence of Chemical Constitution on Adsorption of Dyes by the Insoluble Part of Heat-dehydrated Gum Arabic. J. S. Behrana and C. S. Narwani. *J. Indian Chem. Soc.*, **28**, 252–256 (May 1951).

Insoluble gum arabic (obtained by heating gum arabic at 165–170°c.) irreversibly adsorbs basic dyes, exchanging Ca ions for basic dye ions. In presence of NaCl, however, the basic dyes are not adsorbed, owing to the preferential exchange of Na ions for Ca ions. Freundlich's isotherm is followed only in the case of Malachite Green. Acid dyes, with the exception of Congo Red in very dilute solutions, are not adsorbed. C. H. R.

PATENTS

Backing Sheets for Thermoplastic Transfers. American Viscose Corpn. *USP* 2,556,078

Rapid transfer is obtained if between the transfer film and the backing there is an intermediate coating of softening point higher than that of the transfer film, this intermediate coating being non-transferable. A thermosetting film-forming resin in the non-thermoplastic insoluble stage is a suitable material for such an intermediate coating. C. O. C.

Colour Photography. Ilford. *BP* 661,211

Methods and material for obtaining corrected colour images are described. C. O. C.

Dyeing and Printing Cellulose Esters and Ethers (VIII p. 75).

Colouring Cloth with Aqueous Pigment–Lacquer Emulsions (VIII p. 75).

X—SIZING AND FINISHING

Urea–Formaldehyde Resins—Use of Alkaline Catalysts in Curing. D. D. Gagliardi. *Amer. Dyestuff Rep.*, **40**, P 769–P 773 (26 Nov. 1951).

Experiments are described in which alkaline substances, particularly $NaHCO_3$, are used as curing catalysts in urea–formaldehyde resin treatments. Although slightly less polymer adheres to the finished material, both durable crease-proofing and stabilisation are obtained. J. W. B.

Yellowing of Acetate Rayon sized with Linseed Oil. P. Poular. *Rayonne*, **4**, (7), 39–41 (1948): *Chem. Abs.*, **45**, 9272 (25 Oct. 1951).

The yellow compound is probably formed by the action of the NH_3 in the air and is either an enolic salt of the keto acids formed by initial oxidation of the oil, or a quinonoid type of compound formed by intermolecular aldol condensation of these acids. Keeping the goods wrapped up prevents this yellowing. C. O. C.

Modification of Wool by Application of Linear Synthetic Polyamides. II—*N*-Hydroxymethylpolyamides. D. L. C. Jackson. *Text. Research J.*, **21**, 655–659 (Sept. 1951).

The effect of surface deposits of *N*-hydroxymethylpolyhexamethylenesadipamide on the felting shrinkage of wool has been determined. The polymer itself is not very effective in preventing felting shrinkage, it being necessary to apply the substituted polymer first and then hydrolyse it on the fibre. A deposit of approx. 3% by weight of polymer on the fabric has been found to eliminate entirely felting shrinkage under the test conditions. The optimum degree of substitution of the polyamide for production of non-feltability is similar to that found for the *N*-methoxymethyl derivatives, i.e. 20–25% –NH– groups substituted. A. B.

Modification of Wool with β-Propiolactone. I—The Chemistry of the Reaction. II—Effect on Rate and Degree of Felting. H. W. Jones and H. P. Lundgren. *Text. Research J.*, **21**, 620–634 (Sept. 1951).

I—β-Propiolactone, dissolved in organic solvents or applied as the vapour, reacts with wool to give a product of greatly different chemical and physical properties, including a marked alteration in felting properties, a somewhat greater lustre, and a softer and whiter fibre. Investigation indicates that the reaction involves initial attachment at histidine, methionine, cystine, and lysine, and possibly glutamic acid, serine, and threonine. This initial reaction is probably followed by an "anchored" polymerisation at these sites. The modified wools absorb much less water than untreated wool under the same conditions.

II—The effect of modification with β-propiolactone on the rate and degree of felting of loose wool is described. Maximum effect is obtained at 40–60% by weight uptake of propiolactone. The dry felts from modified wool have a high degree of hardness, split resistance, and tensile strength, and the wet felts are softer and more pliable than untreated wool felts. A. B.

PATENTS

Imparting Permanent Crimp to Nylon Threads. L. A. Billion. *BP* 660,993

Nylon yarn is crimped by twisting tightly, relaxing, heat-setting, back-twisting to a small number of t.p.in., and finally treating with a hot swelling agent, e.g. treating in slightly alkaline water at 80°c. for 30 min. This last operation may be carried out after the yarn has been made into fabric. C. O. C.

Laundry Bag. Celanese Corpn. of America. *USP* 2,555,561

Fabric of high-tenacity saponified acetate rayon is rendered stronger and more resistant to laundering agents by treating it with an 8% aqueous solution of NaOH at 20°c. for 20 min. C. O. C.

Treating Textiles with Condensates of Polyhydric Alcohols and Ketones with Aldehydes. Dan River Mills. *BP* 661,376

Starch methylol (obtained by treating starch with formaldehyde in presence of alkali) polymerises or condenses with acetone methylol (obtained by treating acetone with formaldehyde in presence of alkali) to form a colourless starch–formaldehyde–acetone copolymer or condensate. When this condensate is applied to cellulosic textiles in presence of a mild alkaline catalyst, it reacts with the fibres to produce cellulose ethers. The effect produced by formation of these cellulose ethers varies according to the components (and their proportions) in the condensate used. Thus maximum dimensional stability is obtained by use of 1 part by weight of starch methylol to 3 parts of acetone methylol. C. O. C.

Improving the Adhesion of Rubber to Cellulosic Fibres. Callaway Mills Co. *USP* 2,555,304

Better adhesion is obtained if the fibres are first treated with dialkyl esters of an αβ-unsat. dicarboxylic acid, e.g. diethyl maleate. C. O. C.

Producing Insoluble Coatings from Starch Ether-Carboxylic Acids and/or Starch Ester-Carboxylic Acids. W. A. Scholten's Chemische Fabrieken. *BP* 661,278

Insoluble coatings are obtained, e.g. on textiles, by producing *in situ* a water-insoluble multivalent metal salt of a starch ether carboxylic acid and/or a starch ester carboxylic acid, e.g. by double decomposition of a solution of a salt of such an acid which dissolves or swells in water and of a solution of a multivalent metal salt. *BP* 661,277

If a ferrous salt is used, it may be applied simultaneously with the solution of the starch derivative, an insoluble ferric compound then being formed by oxidation. C. O. C.

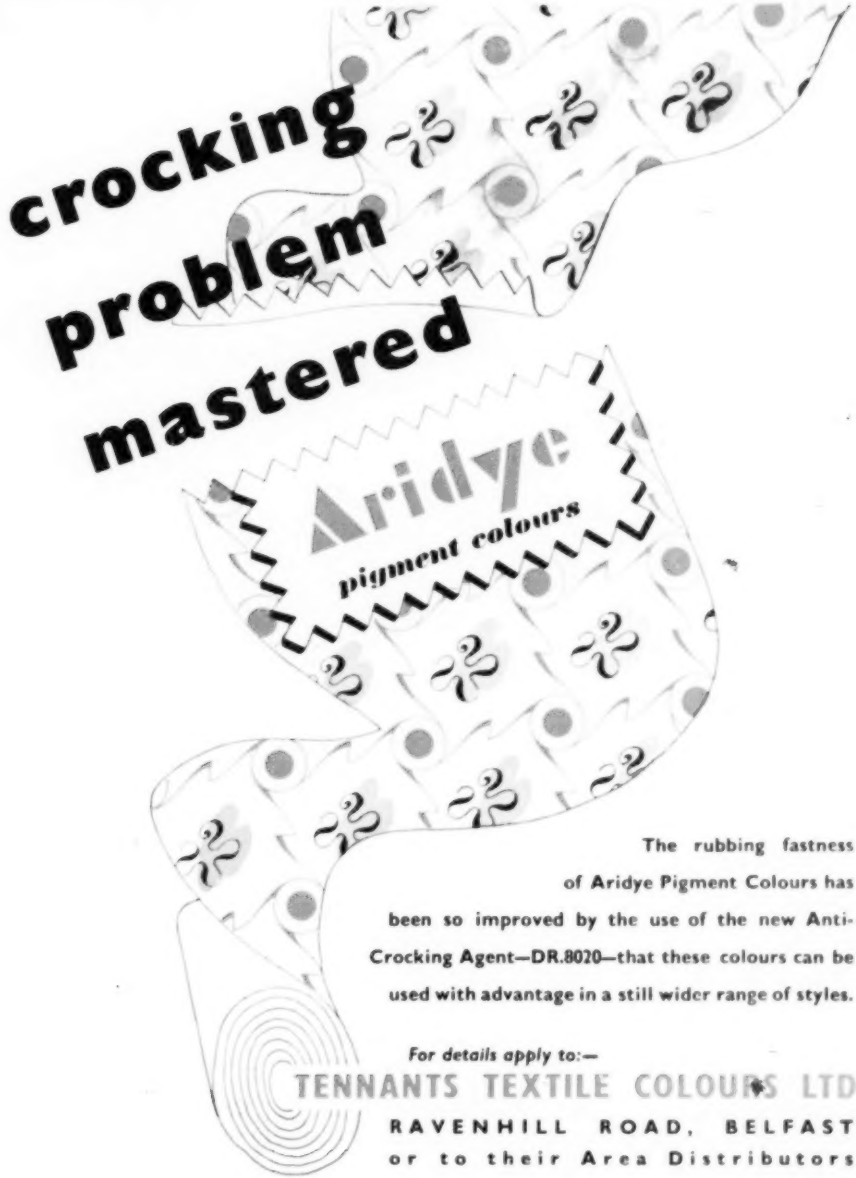
Static Electrification of Nylon—Reduction by Inhibitors (VI p. 74).

Dynel Fabrics—Dyeing and Wet Finishing (VIII p. 75).

XIV—ANALYSIS; TESTING; APPARATUS

Studies on Coal-tar Colours. IX—Preparation, Purification, and Determination of D&C Yellow No. 7, D&C Orange No. 5, D&C Red No. 21, Tetrachlorofluorescein, D&C Red No. 27, and FD&C Red No. 3 (IV p. 72).

Colour and Constitution. XI—Anhydronium Bases of p-Hydroxystyryl Dyes as Solvent Polarity Indicators (IV p. 73).



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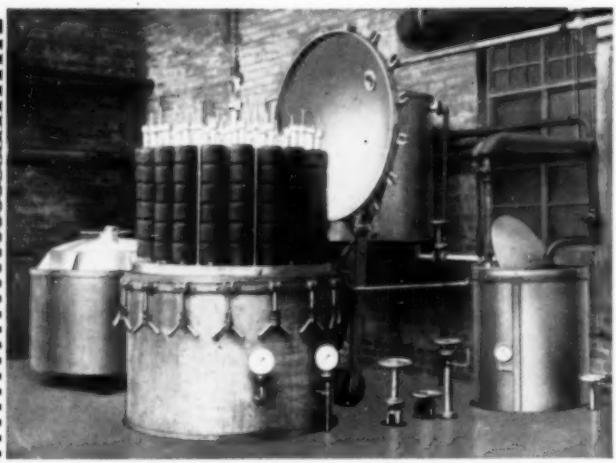

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FORTHCOMING MEETINGS OF THE SOCIETY—*continued*

LEEDS JUNIOR BRANCH

All meetings to be held in the Colour Chemistry Lecture Theatre, Leeds University, at 4 p.m.

1952

Tuesday 26th Feb. — Dr. F. L. Warburton (Wool Industries Research Association) *Colour Vision*

MANCHESTER JUNIOR BRANCH

All meetings commence at 6.30 p.m.

1952

Friday 14th Mar. — Lecturer from the Bleachers' Association Ltd. Name later. *Progress in Textile Bleaching.* Reynold's Hall, College of Technology, Manchester

WEST RIDING SECTION

All meetings held at the Great Northern Victoria Hotel, Bradford, at 7.15 p.m. unless otherwise stated

1952

Thursday 28th Feb. — Dr. A. S. C. Lawrence (Dept. of Chemistry The University, Sheffield) *Detergents* (exact title later)

Tuesday 4th March — T. Thorne Baker, Esq. (Director of Research, Dane & Co. Ltd.) *Fluorescent Dyestuffs and the Application of Fluorescent Textiles.* Metropole Hotel, Leeds

Thursday 13th March — R. J. Hannay Esq., B.Sc., F.R.I.C., W. H. Major Esq., M.A., and R. Pickin Esq. (Brotherton & Co. Ltd.) *A New Method of pH Control in Dyeing and some observations on the Metachrome Process*

Thursday 27th March — ANNUAL GENERAL MEETING

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Persons desirous of joining the Society as Ordinary Members or Junior Members may obtain Application Forms from the General Secretary, or from the Honorary Secretary of any Section of the Society

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All inquiries relating to Advertisements in the Journal should be addressed to the General Secretary, The Society of Dyers and Colourists, Ocean Chambers, 19 Piccadilly, Bradford, Yorks.

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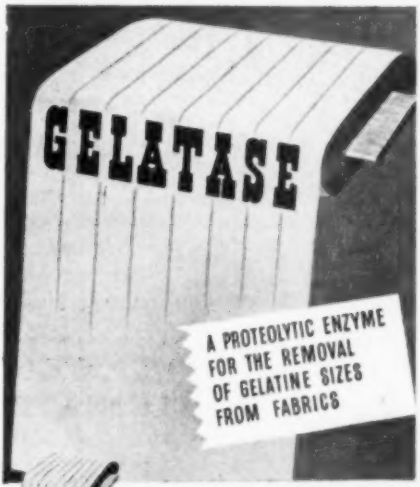

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